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THE MANUFACTURE OF ARTIFICIAL SILK

THE MANUFACTURE OF ARTIFICIAL SILK

WITH SPECIAL REFERENCE TO
THE VISCOSE PROCESS

BY

E. WHEELER

M.B.E., A.C.G.I., A.I.C.

WITH A FOREWORD

BY

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BEING VOLUME ONE OF A SERIES OF
MONOGRAPHS ON APPLIED CHEMISTRY

UNDER THE EDITORSHIP OF

E. HOWARD TRIPP, PH.D.

NEW YORK

D. VAN NOSTRAND COMPANY

1928

677.4
W56m
288375

Printed in Great Britain.

EDITORIAL PREFACE

In these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date ; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place ; and to these many will add the growth of our sense of " values." The value of new work in science varies greatly : the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes : he must pick out the plums

to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. Howard Tripp.

London,
October, 1927.

FOREWORD

By Sir William J. Pope, K.B.E., D.Sc., LL.D., F.R.S.

The art of manufacturing an artificial fibre having useful applications in the textile industries was in its infancy at the opening of the present century; although a number of enthusiastic early workers foresaw its rapid development, it gave to the instructed general public little promise of becoming so soon what it is to-day, the basis of great technical and commercial enterprises. Artificial fibres are now being made on an industrial scale which has involved vast capital expenditure; armies of workers are now employed in invention, development and manufacture connected with artificial silk, and the patent literature relating to the subject is of formidable bulk. It is already clear that the present production, large as it is, represents but a small fraction of what the textile industries of the world will be capable of absorbing as further inevitable progress plays its part. The new industry is distinguished by certain peculiarities from several others which have risen to importance during very recent years.

Firstly, whilst it presents itself as an auxiliary to the staple textile industries dealing with animal and vegetable fibres, centuries of inventive activity have doubtless ensured that future developments in the spinning and weaving of the natural fibres, such as silk, cotton and wool, will necessarily be slow. It would seem to follow that improvements in the manufacture and application of artificial fibres, which are certain to be made with ever increasing rapidity, will ultimately raise the artificial fibre from the rank of an auxiliary to the natural fibres to that of a powerful competitor with them.

Secondly, the development of the new industry has, undoubtedly, been retarded by the meagre scope of our chemical knowledge of the various forms of cellulose which constitute the raw material of the artificial fibre. Notwithstanding the valuable contributions of many able pioneers, our knowledge of the chemical constitution of the celluloses remains still in an elementary stage; our understanding of the mechanism of the chemical reactions to which the celluloses are subject is perhaps even more rudimentary. The investigation of the chemistry of the celluloses is beset by experimental difficulties which have hitherto baffled the organic and physical chemist; we are only now beginning to discern dimly certain main lines of research which may be fruitful. Up to the present, therefore, progress has been achieved largely through empirical means, and the best methods for preparing and treating the solutions for spinning have been worked out chiefly by experiment of the trial and error type. The time must come, and may indeed be near, when the chemical and physical factors which govern the viscosity of the spinning solutions and the tensile properties of the resulting fibre will be well understood; that knowledge, supplemented by the mechanical ingenuity which has been already expended lavishly in the device of spinning machinery, will indubitably lead to products far more valuable as textile components than are the artificial fibres of to-day.

Such a field of investigation as this—which has already yielded results of great technical importance and which offers wide prospects for future progress—is naturally attracting the attention of many chemists and engineers. Its profitable cultivation calls for a preliminary and extensive survey of what has been already achieved. For this reason Mr. Wheeler's little work will find a cordial welcome.

CAMBRIDGE,
November, 1927.

AUTHOR'S PREFACE

THE keen interest with which recent developments in the artificial-silk industry have been followed by the investing public has drawn attention to the technicalities of the different processes that are used. Until a few years ago, few details were available outside the patent literature and a few technical papers ; at the present time the technical literature is much more voluminous and separate journals are devoted entirely to the industry in Germany and the United States. The present monograph cannot claim to be an exhaustive treatise on the subject, but its object is to present a description of the essential chemical and engineering details of the modern methods of manufacturing, and of the properties and uses, of artificial silk.

The artificial-silk industry has developed very rapidly, and, as the result of experience, new and improved methods are continually being introduced ; these may or may not survive the test of time. Such developments, in so far as they are indicated from the patent literature, are referred to in the text.

In conclusion, I should like to express my thanks to the following firms who have supplied plates, blocks or photographs of the figures referred to, together with technical information :—

John Hetherington & Sons, Ltd., Manchester. (Figs. 2, 6, 19B and 29.)
Baker, Perkins, Ltd., Peterborough. (Fig. 3.)
Dobson & Barlow, Ltd., Bolton. (Figs. 4, 5, 7, 21A, 21B, and 25.)
Horology, Ltd., London. (Fig. 11.)
C. Macintosh & Co., Ltd., Manchester. (Fig. 13.)
Derby & Co., Ltd. (Fig. 15.)
Carl Hamel, of Chemnitz. (Fig. 22.)

Joseph Stubbs, Ltd., Manchester. (Fig. 23.)
Tomlinsons (Rochdale), Ltd. (Figs. 26 and 28.)
Manlove, Alliott & Co., Ltd. (Fig. 30.)
Goodbrand & Co., Ltd., Stalybridge. (Figs. 42 and 50.)

I am also much indebted to the following individuals and firms :—

Dr. E. F. Armstrong, F.R.S., Mr. R. S. Horsfall and British Dyestuffs Corporation, Ltd., Dr. J. Thomas, F.I.C., and Scottish Dyes, Ltd., and The Clayton Aniline Co., Ltd., for information concerning the dyeing of artificial silk incorporated in Chapter XI., to Mr. P. E. King, A.I.C., of Leeds University, for the photomicrographs (Figs. 36A–G, 37A and B, 38A and B, 39A–C, 40, 46A and B), and to Mr. Hugh Griffiths, B.Sc., for certain information on artificial-silk spinning machinery.

E. WHEELER.

HARROW,
November, 1927.

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THE MANUFACTURE OF ARTIFICIAL SILK

CHAPTER I

INTRODUCTORY AND HISTORICAL

ANY account of the outstanding advances in the technical application of scientific discoveries of the last three decades would perforce include reference to the motor car, wireless telegraphy and telephony, and perhaps artificial silk.* Though the last-named has, in its spectacular aspects, only recently been brought before the public eye, yet the development of the artificial-silk industry constitutes one of the most interesting features in the recent history of chemical engineering and textile technology.

The idea of producing artificial silk was, as Sir William Bragg recently pointed out in a lecture at the Royal Institution (1), put forward as early as 1665 in Hooke's " Micrographia," where it was suggested that " there might be a way found out to make an artificial glutinous composition much resembling, if not full as good, nay better, than that excrement or whatever other substance it be out of which the silk-worm wire-draws his clew " (2). A similar suggestion was put forward in 1734 by the naturalist de Réaumur (3), in an account of the silkworm (*Bombyx Mori*). In support of this idea de Réaumur referred to the drawing out of glass filaments. It may be of interest here to refer

* The term " artificial silk " has been used throughout this book in preference to Rayon, as the latter is not yet sufficiently well known, and is liable to be confused with certain trade names for a particular kind of material. The word " Rayon " is used largely in the United States, and its use has been adopted in this country by the Silk Association (*J. Soc. Chem. Ind.*, 1924, **43**, 1269) ; it was hoped that by the introduction of such a term no confusion would arise between goods made of artificial silk from cellulose (sometimes called art silk) and real silk.

to an account that was given to the Royal Society in 1740, of a Frenchman named Bon, who had actually produced a yarn from the filaments of spiders' webs and made with it stockings and gloves. In 1770, a Frenchman, named Dubet, described in a book some experiments on producing filaments from the silky gum extracted from dead silkworms (4). The idea of extruding certain solutions through fine holes was suggested by Schwabe, a silk manufacturer, in a paper read before the Manchester meeting of the British Association (1842). Audemars of Lausanne in 1855 took out the first English patent (No. 283) for the production of artificial silk from a solution of nitrocellulose in an alcohol-ether mixture by drawing out threads from it with a steel pointer and reeling them.

It was, however, nearly thirty years later, when the application of electricity for lighting purposes directed research to the production of filaments, which could be readily carbonised, from cellulose solutions, before further developments took place in the production of artificial silk. Swann, in 1883, took out a patent (English Patent No. 5,978) for producing filaments from nitrocellulose solutions. Although this was primarily for making carbonised filaments for the electric lamp, yet Swann recognised that such filaments were capable of being used for producing an artificial silk, and samples were exhibited in London in 1884 and 1885 (5). It is interesting to note that Swann denitrated his filaments by using ammonium sulphide.

Other inventors had also been experimenting about the same time with solutions of cellulose in an ammoniacal solution of copper salts, known as Schweitzer's * reagent or cuprammonium solution (6),

* Although Schweizter is usually credited with the discovery of the solvent action of copper-ammonia solutions on cellulose, in the " Life and Labours of John Mercer," by Parnell, reference is made to the fact that Mercer had noticed the same phenomena, and had recovered the cellulose from such a solution by the action of sulphuric acid. Mercer lived from 1791–1866; his discovery may therefore have been prior to that of Schweitzer.

and in zinc chloride, for the production of electric lamp filaments.

On the other hand, Count H. de Chardonnet, in France, had been working on the production of artificial-silk filaments from nitrocellulose solutions. An account of his work was presented in 1884 to the Académie des Sciences, and patents were taken out in 1885 (7). Specimens of cloth woven from such artificial silk were shown at the Paris Exhibition of 1889.

From that time the production of artificial silk by the nitrocellulose or Chardonnet process, as it came to be called, went forward and, after considerable vicissitudes, was established on a manufacturing basis in France, Switzerland, Germany and other countries. Although in recent years this process has been largely superseded by the cheaper viscose process, yet, owing to its special properties, Chardonnet artificial silk is still in demand for some purposes.

As mentioned above, certain inventors had been experimenting with cuprammonium solutions of cellulose. In 1890, Despeissis patented the cuprammonium process for the production of artificial silk (French Patent 203,741); it was, however, not till 1897, when Pauly took up this process, that it was started on a commercial basis. Considerable difficulties had to be overcome, and through his exertions, and those of Urban, Fremery, Bronnert and others, the manufacture of artificial silk by this process became established in France, Germany, Belgium and elsewhere.

While these two processes were coming to the fore, Cross, Bevan and Beadle, working on cellulose, discovered in 1891 that alkaline cellulose reacted with carbon bisulphide to form a compound soluble in water, which they named "viscose" (English Patent No. 8,700 of 1892). The importance of this discovery was not at first realised, but Stearn patented methods for producing filaments from viscose, chiefly for electric lamps (English Patent No. 1,020 of 1898), and Topham developed the centrifugal method of spinning twisted

filaments from cellulose solutions (English Patents Nos. 23,157 and 23,158 of 1900). From that time the viscose process for the production of artificial silk went ahead, and was developed to its present pitch of success by Messrs. Courtaulds in this country.

Another process which has aroused considerable interest in the last few years is based on the spinning of cellulose-acetate filaments. Cellulose acetate was first prepared in 1869 by Schützenberger and Naudin, but, although a considerable amount of research was devoted to its application for artificial-silk production in Germany, its commercial development has only quite recently achieved some measure of success, largely owing to the inventions of H. Dreyfus.

The four processes referred to above are the only ones which at present are used for producing artificial silk commercially. It is, however, by no means certain that the last word has been said on processes for artificial-silk manufacture. Considerable attention is now being directed by Lilienfeldt and others to other compounds of cellulose—for example, the cellulose ethers—and their successful utilisation in this direction is by no means improbable.

The following figures for world production between the four chief processes indicate the developments which have taken place between 1909–1924 (8) :—

	1909	1924
World production of artificial silk in tons	7,400	62,000
	Percentage of World Production.	
Nitrocellulose process	48	7·8
Cuprammonium process	36	1·4
Viscose process	16	88·0
Acetate process	—	2·8

References.

(1) Sir William Bragg. "Old Trades and New Knowledge." Six lectures before the Royal Institution, Christmas, 1925.
(2) *Chemistry and Industry*, 1926, **45**, 221; *Times Artificial Silk Supplement*, April 2, 1927.
(3) de Réaumur. "Mémoires pour servir a l'histoire des insectes," 1734.
(4) La Muriometrie. "Instruction nouvelle sur le lever de la soie," 1770.
(5) *J. Soc. Chem. Ind.*, 1885, **4**, 34; *Engineering*, 1885, **40**, 39.
(6) Schweitzer. *J. für prakt. Chem.*, 1857, **72**, 109.
(7) de Chardonnet. French Patent 165,349; German Patent 38,368 (1885).
(8) V. Hottenroth. "Die Kunstseide," 1926.

Historical accounts of the development of an artificial silk industry will also be found in :—

A. Chaplet. "Les Soies Artificielles," 1926.
Times Artificial Silk Supplement, March 9, 1926.
W. P. Dreaper. Article on Artificial Silk in Thorpe's "Dictionary of Applied Chemistry," Vol. VI., 1926.

CHAPTER II

CHEMISTRY OF ARTIFICIAL SILK MANUFACTURE

THE chemistry of artificial-silk manufacture is the chemistry of cellulose and its derivatives. Although cellulose has been classified as a carbohydrate from the early days of chemistry, yet its constitution has not yet been elucidated. The manufacture, however, of its derivatives has been carried out on a large scale throughout the world for many years.

In so far as research has gone, cellulose is considered to be a polysaccharide, being probably built up of glucose units, and is usually represented by the chemical formula $(C_6H_{10}O_5)_x$, in which x is probably not less than 3 (1). Cellulose is met with in nature as a constituent of cotton (87–91%), the woods (60% cellulose), and the straws (35% cellulose); from the technological point of view cotton and the woods are the most important sources of cellulose for the manufacture of artificial silk at the present day.

Although various theories have been put forward as to the nature of celluloses from different sources, it is becoming recognised that the cellulose isolated from cotton, wood and straw, and freed from its associated combinations and impurities, is identical, differing only in its degree of polymerisation. As a working hypothesis in reviewing its reactions, cellulose can be conveniently considered as bearing some similarity to an aliphatic polyhydric alcohol. Furthermore, cellulose is a product of the plant cell and possesses a fibrous structure. Consequently its behaviour towards chemical reagents can only be explained by taking into account its physical structure and considering it as a colloid.

Cellulose is the raw material for artificial-silk manufacture in the four chief processes which are

being worked successfully at the present day; these four processes are :—

(*a*) Viscose process.
(*b*) Cuprammonium process.
(*c*) Nitrocellulose process.
(*d*) Cellulose-acetate process.

(a) Viscose Process.

When cellulose is treated with sodium hydroxide solutions (2 cellulose : 1 sodium hydroxide) of certain concentrations, it is modified physically (mercerised) and appears to form a compound of the nature of an alcoholate, though the soda-cellulose compound (alkali cellulose) is at once decomposed by excess of water (2). This alkali cellulose reacts with carbon bisulphide to form cellulose xanthate, which dissolves in water to give the so-called viscose solution. Thus

$$* \; C_6H_9O_4 - ONa + CS_2 \rightarrow C(=S)(SNa)(O - C_6H_9O_4)$$

Sodium cellulose xanthate.

An analogous compound is formed from sodium ethylate :

$$C_2H_5\,ONa + CS_2 \rightarrow C(=S)(SNa)(O\,.\,C_2H_5)$$

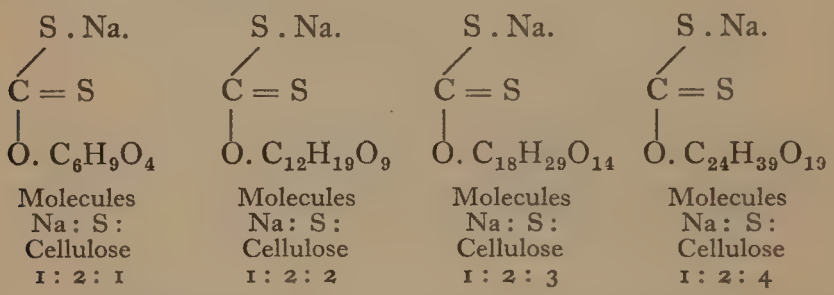
Sodium ethyl xanthate.

At the same time the carbon bisulphide reacts with any excess of soda present to form compounds, such as sodium thiocarbonate and sodium sulphide.

* The unit $C_6H_{10}O_5$ is generally used for convenience in illustrating the reactions of cellulose, although, as already stated, the actual cellulose unit is probably a multiple of it.

The viscose solution is not stable; the dissolved cellulose xanthate gradually changes, splitting off dithiocarbonate residues until finally only cellulose remains. This process is known as the ripening of the viscose and is of considerable importance in the manufacture of artificial silk, as it is necessary to decide at what stage of the ripening the viscose should be spun.

The following scheme approximately indicates the process of ripening :—


S . Na.
C = S
O. $C_6H_9O_4$
Molecules Na : S : Cellulose 1 : 2 : 1
S . Na.
C = S
O. $C_{12}H_{19}O_9$
Molecules Na : S : Cellulose 1 : 2 : 2
S . Na.
C = S
O. $C_{18}H_{29}O_{14}$
Molecules Na : S : Cellulose 1 : 2 : 3
S . Na.
C = S
O. $C_{24}H_{39}O_{19}$
Molecules Na : S : Cellulose 1 : 2 : 4

The splitting off of the dithiocarbonate residues gradually gives rise to an increased formation of by-products, such as sulphides and thiocarbonates, formed by interaction with the free soda present. The rate of ripening varies directly with the temperature, and is influenced by the addition of inorganic and organic compounds to the viscose. As the ratio of cellulose to combined sulphur increases the degree of solubility of the cellulose xanthate diminishes, until finally insolubility is reached. It has been found that the solubility of the cellulose xanthate depends partly on the proportion of free alkali present. Tests for ascertaining the degree of ripeness of the viscose have been devised that are based on the amount of certain salt solutions of definite strength required to precipitate the cellulose xanthate from solution at different stages of the ripening period (see p. 137).

It should also be borne in mind that viscose is a colloidal solution, and consequently the chemical changes referred to above must be considered in the

light of this fact. Some writers have even ascribed the whole of the ripening action of viscose as due to colloidal changes, but this hypothesis cannot be accepted in view of the very definite chemical evidence to the contrary (3).

In practice the viscose solution is spun at a definite stage of ripening, and before the cellulose xanthate becomes insoluble, into precipitating baths of acids and salts, so that the cellulose is immediately regenerated, and the xanthate residue is decomposed to sulphuretted hydrogen, sulphur, and carbon bisulphide. The regenerated cellulose possesses increased chemical activity (*e.g.*, copper-reduction figure) and is probably less polymerised than the original cellulose.

The further chemical reactions involved in the viscose process consist in the purification of the regenerated cellulose thread by washing free from acid, removal of the sulphur by sodium sulphide solution, and oxidation of the impurities by sodium hypochlorite solution (bleaching).

(b) Cuprammonium Process.

Cellulose, when steeped under certain specified conditions in ammoniacal solutions of copper oxide, is gradually dissolved or dispersed. Various theories have been put forward to account for this solvent action, but the nature of such a solution is still not very clear. Probably the cellulose forms an adsorption compound with the copper compound.

One of the most recent theories advanced assumes the formation of a complex copper-cellulose anion which forms a stable salt with the copper ammine as kation, *e.g.*, $(C_9H_7O_5Cu)_2 . Cu(NH_3)_4$. (4).

The cuprammonium solution is not very stable; the changes which it undergoes, however, are very slow, the chief being oxidation and a gradual depolymerisation of the cellulose, as shown by a decrease in viscosity. The cellulose is regenerated from the solution by projecting it into alkaline or acid precipi-

tating baths, removing the copper, and purifying the cellulose by bleaching.

(c) Nitrocellulose Process.

The nitrocelluloses or cellulose nitrates are the oldest known derivatives of cellulose, and constitute one of the principal products of the explosives industry.

The compounds produced by the action of nitric acid on cellulose cannot, however, be sharply defined like the esters of aliphatic alcohols, *e.g.*, nitroglycerin.

The cellulose nitrates still retain their fibrous structure and behave as colloids. They cannot, therefore, be purified by crystallisation or distillation. Under the optimum conditions of esterification a compound containing a maximum of 14·17 % nitrogen is obtained, which can be considered as a tri-, hexa- or dodeca-nitrate, etc., according as the cellulose complex is considered to be made up of one, two, three or more of the unit molecules $C_6H_{10}O_5$.

By varying the conditions of nitration, *i.e.*, time and temperature of reaction, composition of nitrating mixture in nitric acid, sulphuric acid and water, compounds with different percentages of nitrogen can be obtained that contain up to the maximum amount of 14·17% nitrogen. Cellulose nitrates containing 12·5% nitrogen and over are insoluble in ether-alcohol and constitute the guncottons ; they are, however, of no interest from the point of view of artificial silk. For the latter, cellulose nitrates which have a nitrogen content of 11·3–12·5% nitrogen, and are soluble in ether-alcohol mixtures, are used (known as collodion cotton). These cellulose nitrates probably consist of mixtures of mono-, di- and tri-nitrates.* It must be pointed out that in the course of nitration a considerable number of side reactions may take place which influence the final product. Thus the sulphuric acid forms esters with the cellulose, while the nitric acid

* Referred to the unit molecule.

exerts an oxidising action on the cellulose, and both acids may hydrolyse the esters formed. All these factors have to be taken into account in considering the formation of cellulose nitrates.

The cellulose nitrate for artificial-silk manufacture is usually dissolved in an ether-alcohol mixture and spun as a thread of cellulose nitrate. In this connection it may be pointed out that a considerable amount of research work has been carried out on the viscosity of solutions of cellulose nitrates in mixed solvents, chiefly from the point of view of studying the colloidal state of the ester in solution and the influence of various solvents (5).

The thread has next to be saponified (denitrated), a process which is carried out by hydrolysing with sodium hydrosulphide. By this means cellulose is regenerated with apparently little alteration. The cellulose, however, shows by its properties, such as increased absorptive power towards dyestuffs and higher copper-reduction figure, that some modification or depolymerisation of the original cellulose has taken place, the extent of which depends on the conditions of the esterification.

(d) Acetyl-Cellulose or Cellulose-Acetate Process.

The formation of acetates of cellulose by the action of acetic anhydride, or even of acetic acid on cotton, has been known for a long time, but a considerable amount of confusion has existed as to the number of acetyl groups that can be introduced in the cellulose molecule. It appears, however, now to be clear that, as in the case of nitric acid esters, only three hydroxyl groups per cellulose unit ($C_6H_{10}O_5$) can be esterified, and that the existence of higher acetates must be ascribed to degradation or acetolysis of the cellulose, whereby lower carbohydrates having more hydroxyl groups are produced.

The acetylation of cellulose by acetic anhydride takes place readily in the presence of suitable dehy-

drating catalysts, such as zinc chloride and sulphuric acid, giving rise always to the tri-acetate, provided the conditions of the reaction are carefully controlled. The tri-acetate thus obtained is insoluble in acetone, but soluble in chloroform. For artificial-silk manufacture the tri-acetate as such is not used, but an acetate containing about 52·5–48·7% of acetyl, *i.e.*, a compound containing a certain amount of the tri-acetate mixed with possibly a certain amount of the mono- and di-acetates that are soluble in acetone. This technical product is obtained by the so-called hydration of the tri-acetate, whereby a certain degree of acetolysis and hydration takes place. The conditions can be carefully controlled, so that a uniform technical product is obtained, which, however, has not as yet been chemically defined.

The acetone-soluble cellulose acetate is usually spun from an acetone solution into artificial silk, as will be described in a later chapter. It is, however, of interest to point out that the artificial silk therefrom is actually cellulose acetate, and comes into use as such; it is not cellulose, as are all the other commercially important artificial silks.

We have so far only referred in this chapter to the four chief processes of producing artificial silk to-day. It might, however, be pointed out that there are other organic esters of cellulose known—for example, formates, benzoates, butyrates, nitro-acetates—some of which may in the future become important for artificial silk manufacture.

Another series of compounds, which from the chemical side is of considerable interest in relation to the constitution of cellulose, is the cellulose ethers, the technical application of which has only just begun.

One of the early solvents of cellulose was zinc chloride, which was used for producing the filaments of incandescent electric lamps. Its use for the production of artificial silk had not much success, chiefly

owing to the hydrolytic action of the zinc chloride on the cellulose and consequent poor quality of the resulting artificial silk.

A few years ago the use of inorganic salts of thiocyanic acids as solvents or dispersing agents for cellulose attracted some attention, but their application to artificial-silk manufacture has so far proved unsuccessful. It is not possible in a book of this nature to deal fully with the chemistry of the cellulose compounds. The reader who wishes to study the subject more fully is referred to the works on cellulose listed below.

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CHAPTER III

VISCOSE PROCESS. I

1. Preparation of the Solution

THE chemical reactions involved in the preparation of viscose having been briefly discussed in the last chapter, it is now proposed to describe the methods by which these reactions are carried out in a modern viscose factory. It is not possible in a work of this kind to describe in detail every process or modification of a process for making viscose which has been patented or suggested from time to time. Moreover, as is well known in other chemical processes, the same result may often be attained equally well by different methods. These remarks apply particularly to the preparation and spinning of viscose solutions, for which the most extravagant claims have been made as to the beneficial effects of particular variations in manufacture.

The flow-sheet reproduced on the next page clearly indicates the different stages and operations in the manufacture of the viscose solution before it reaches the spinning machine. These stages and operations will now be dealt with *seriatim* :—

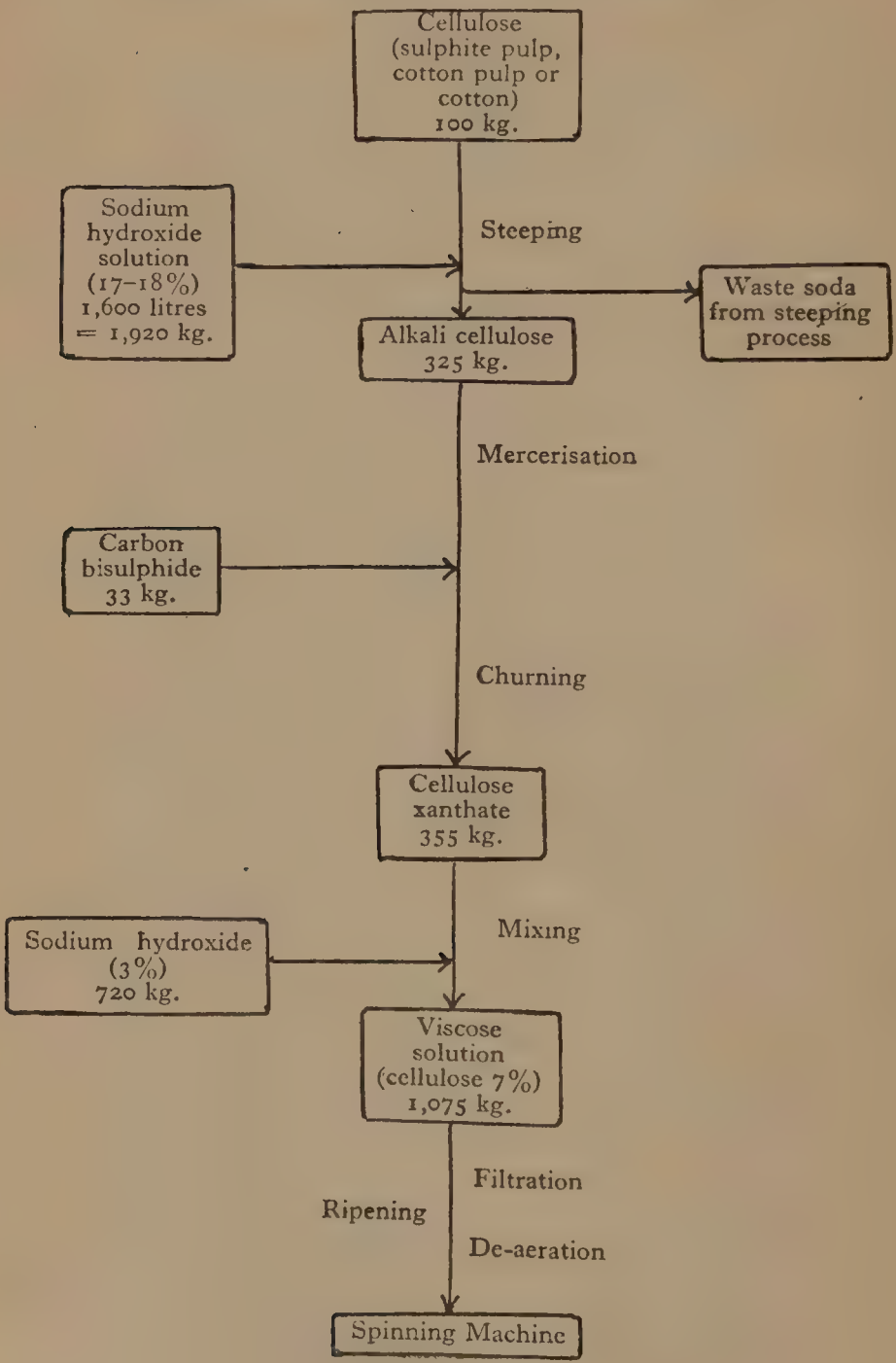
Raw Materials.

Cellulose.—At present only cotton and wood come into consideration as sources of cellulose for viscose manufacture.*

Cotton in the form of spinning waste and linters (short cotton fibre unspun) can be utilised, but its use

* The question of using other forms of cellulose, such as flax and esparto, has recently been mooted. Their successful utilisation will depend on production cost and quality of the artificial silk produced therefrom.

Flow-Sheet for Viscose Process I.



for viscose has hitherto not been very extensive, chiefly owing to the fact that cellulose isolated from wood is a much cheaper raw material and can be handled more economically.* Cotton has, however, an advantage in that the artificial silk produced from it has at least 25% greater tensile strength than that produced from wood. Cotton, before it can be used, has to be freed from oil, fat, wax and colouring matter by extraction with organic solvents, boiling under slight pressure with weak alkalies, scouring and bleaching (see Chapter VII.). The purified material, after drying and teasing out, is ready for use, or may be pulped and converted into sheets, in which form it is more easily handled.

The other principal form of cellulose used for viscose manufacture is isolated from certain woods, such as spruce, fir and hemlock, by digestion and treatment with certain chemicals (calcium bisulphite solutions), and comes on the market as bleached sulphite wood-pulp. There are other processes for the isolation of cellulose from woods (soda and sulphate processes), but the sulphite pulp has so far been found to be the most satisfactory in the manufacture of viscose, owing to the fact that it contains a higher percentage of cellulose and is freer from associated impurities, such as lignin, than the cellulose isolated by the other methods. Special attention has been paid by the pulp manufacturers to the requirements of the artificial-silk industry.

The sulphite pulp comes into the market in the form of thin cardboard-like sheets measuring about 32 by 24 inches. In the following table are given typical analyses of purified cotton and sulphite pulp supplied for artificial-silk manufacture. For comparison are given the limiting figures usually specified for sulphite pulp for such use (Hottenroth). It, however, does not follow that a pulp giving figures within these limits is

* Sulphite wood-pulp costs at present 2*d*. per lb., as against 5*d*. per lb. for cotton waste or linters.

suitable for viscose manufacture. This can only be determined by actual trial.

Pulp.	Moisture.	α-Cellulose on dry pulp.	Soluble in strong caustic soda.		Resin on dry pulp.	Ash on dry pulp.
			β-Cellulose on dry pulp.	γ-Cellulose on dry pulp.		
	%	%	%	%	%	%
1	7·8	86·7	5·3	6·8	1·18	0·37
2	10·4	80·0	10·4	7·5	0·93	0·43
3	11·0	86·5	12·6		0·39	0·5
4	8·3	87·0	7·2	4·8	0·61	0·35
5*	—	89·3	2·7	7·4	0·88	0·28
Limits for sulphite wood-pulp.	8–12	85–89	11—14		0·6–0·7	0·15–0·3
Cotton*	—	98·0	1·80		0·34	0·12

* Luft. *Die Kunstseide*, 1927, **9**, 92.

It will be noticed that figures are given for α-, β- and γ-cellulose. These forms of cellulose are differentiated by the action of sodium hydroxide solutions (mercerising strength, generally 17·5% NaOH). The β- and γ-celluloses are soluble in such a soda solution and are of no use for viscose manufacture. The α-cellulose represents the most resistant form, and is insoluble in the sodium hydroxide solution; the β-cellulose is precipitated from the solution on neutralisation of the soda, but the γ-cellulose still remains in solution.

Sodium Hydroxide and Carbon Bisulphide.—The only other raw materials required in the manufacture of viscose solution are sodium hydroxide and carbon bisulphide. The former can be easily obtained of a

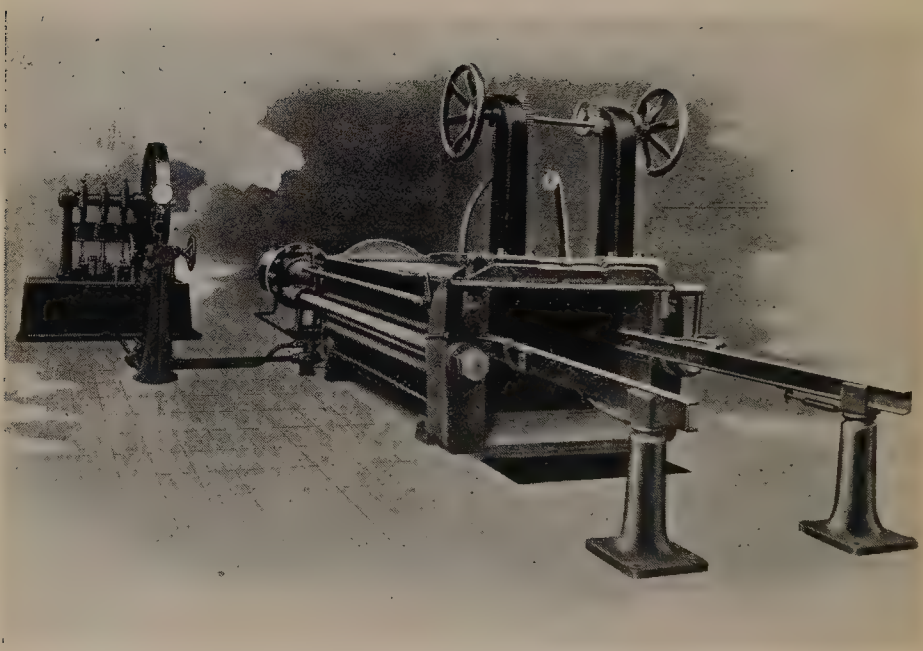


FIG. 2.—Steeping and Pressing Tank.

(*John Hetherington & Sons, Ltd., Manchester.*)

[*To face p.* 19.

high degree of purity, and the following are the permissible limits usually specified for soda content and impurities :—

NaOH . . .	97 %	Should not fall below this figure.
Na_2CO_3 . . .	1 %	Should not exceed these figures.
NaCl . . .	1·25 %	

Carbon bisulphide should be free from sulphur and sulphuretted hydrogen.

Production of Alkali Cellulose.

Steeping.—In order to convert the cellulose into alkali cellulose, the sheets of wood- or cotton-pulp (or cotton, when used) are either immersed in or kneaded up with the sodium hydroxide solution (17–18·5% NaOH). The former method is now generally used, and is carried out in the following manner :—

The sheets, cut if necessary to a convenient size, are placed on edge in a rectangular tank, every 100 sheets or less being separated by thin perforated iron plates. Sufficient room has to be allowed for the swelling of the sheets and escape of the air, otherwise the soda solution may not penetrate evenly into the pulp.

In English Patent 178,152, Dreaper proposes to get over this difficulty by carrying out the steeping operation in vacuum below 5° C., in order to ensure more even steeping and less swelling of the pulp. It has recently been stated that steeping in a vacuum enables the time of steeping to be cut down by 25%, owing to the rapid penetration of the soda.

The steeping is usually carried out at normal temperatures (15°–20° C.),* and for two to four hours.

* The temperatures quoted represent the limits met with in different factories. The temperature adopted in any particular factory is usually kept within ± 1° C.

Pressing.—At the end of this period the soda is drained off and the soaked sheets pressed to about 3–3·5 times their original weight. Thus a batch of 100 kg. of air-dry material, steeped in 1,600 litres of 17·5% caustic soda solution, is pressed to 300–350 kg.

In modern practice the whole operation of steeping and pressing is carried out in a combined plant (English Patent 7,893/1912) (see Fig. 1). The sheets of wood-pulp are placed in the spaces marked (*c*), separated by iron sheets (E). At the end of the steeping operation the soda is run off at K and the ram F, operated by hydraulic pressure, moves forwaid to a given mark and compresses the soaked wood-pulp to the required weight. An illustration of an up-to-date steeping unit

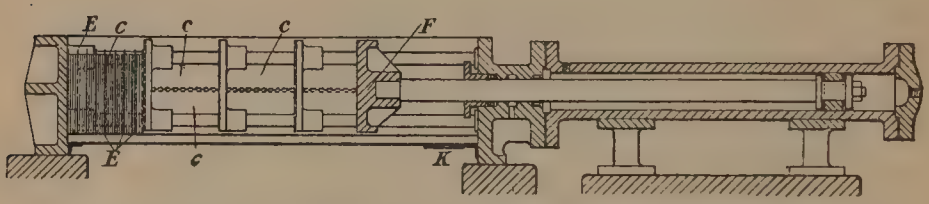


FIG. 1.—Sectional Elevation of Combined Steeping and Pressing Tank. (*English Patent* 7,893 *of* 1912.)

based on this principle is shown in Fig. 2, facing p. 19. Such an installation is capable of dealing with 100–200 kg. of dry wood-pulp at a time.

The waste liquor run off contains the soluble β- and γ-celluloses. It is found in practice that this liquor can be strengthened with 40–45% caustic soda solution and used again, but the amount of soluble cellulose should not be allowed to exceed 1–1·5%, as otherwise its presence in excess will be harmful to the viscose and artificial silk produced therefrom.

Disintegrating.—After the steeped pulp has been pressed it is transferred to a water-jacketed disintegrating or kneading machine (Fig. 3), whereby it is converted into a loose bread-crumb-like material. This machine contains two serrated moveable arms which revolve slowly and exert a certain rubbing and kneading

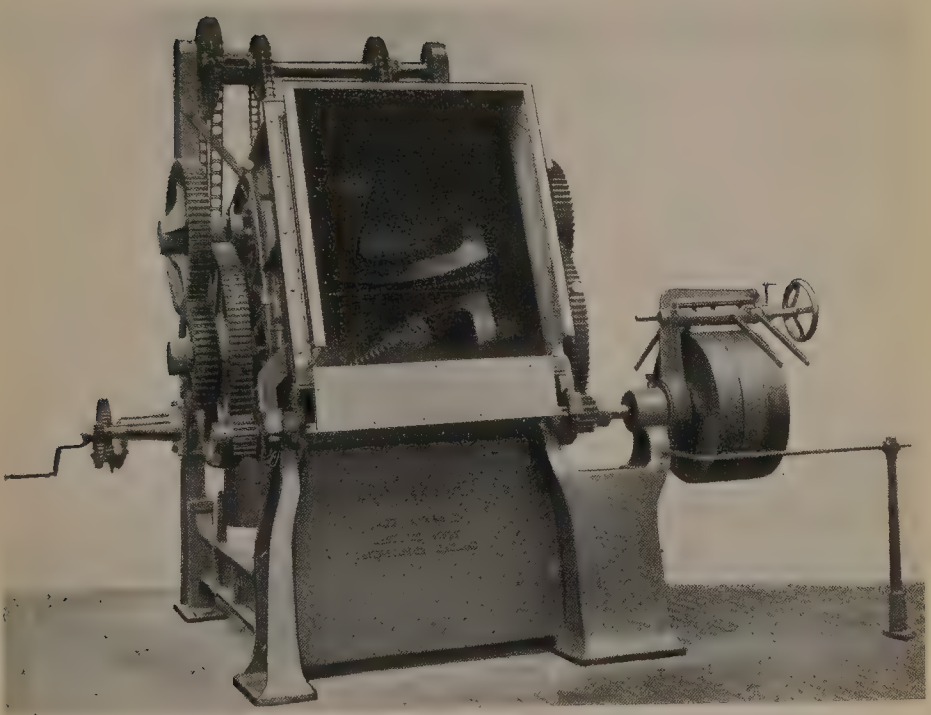


FIG. 3.—Kneading or Pulping Machine for Alkali-cellulose.
(Capacity, 29·3 cub. ft. or 800 litres.)

(*Baker Perkins, Ltd., Peterborough.*)

[*To face p.* 20.

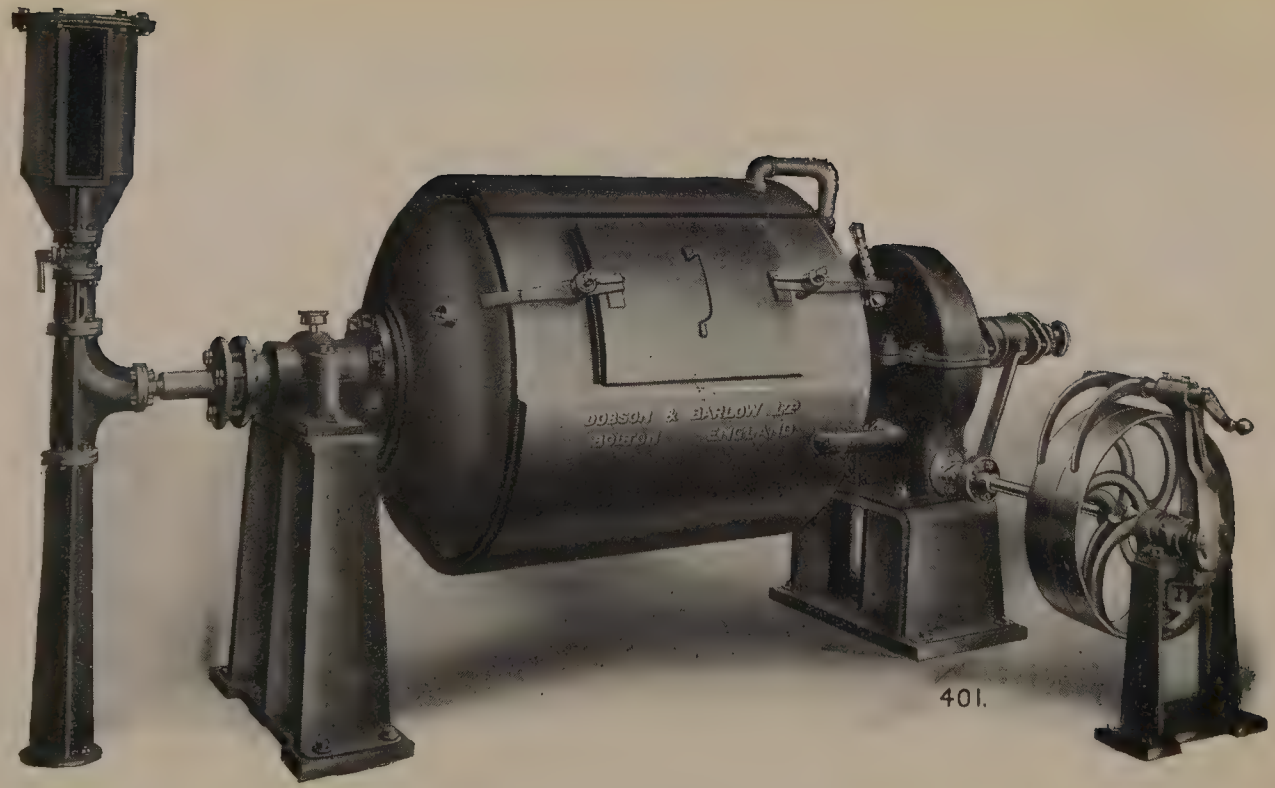


FIG. 4.—Sulphide Drum or Churn.

(*Dobson and Barlow, Ltd., Bolton.*)

[*To face p.* 21.

action, and so produce a very loose, light material. This operation may take two to three hours, according to the charge in the machine, and is usually carried out at a constant temperature (18°–22° C.).

The crumbs of alkali cellulose thus produced should not weigh more than 225–235 gm. per litre, and should have the following composition :—

α-Cellulose	26–27%
NaOH	15–16%
Na_2CO_3	0·3– 1%

Mercerisation or Maturation.—After removal from the disintegrating machine the alkali cellulose is placed in covered bins (10 gallons) and kept at 20°–25° C. for forty-eight to seventy-two hours. The temperature and time will depend on the cellulose used. During this period of maturation oxygen is absorbed and a depolymerisation of the cellulose takes place, so that by suitable regulation of the time and/or temperature any required viscosity of the viscose made therefrom can, within limits, be attained. It has been found that by adding certain oxides or hydroxides to the steeping liquor the rate of oxygen absorption can be increased and the maturation time so reduced (English Patents 13,055 and 14,675 of 1914).

Formation of Cellulose Xanthate.

Churning.—At the termination of the mercerising period the alkali cellulose is transferred to a sulphide drum or churn (also known as a Barratte) for treatment with carbon bisulphide. This apparatus consists of a round or hexagonal iron cylinder, which is rotated slowly (two to three revolutions per minute) about its horizontal axis (see Fig. 4). It is double-jacketed to allow for cooling by water, and provision is made for the introduction of the carbon bisulphide at the side by a pipe passing through the axis of the churn. The churn is usually of about 1,200 litres capacity, and is suitable for a charge of 325 kg. of alkali cellulose,

as it is found necessary to allow about 30% free space, the alkali cellulose occupying about 920 litres.

From 30 to 32 kg. of carbon bisulphide * are slowly added to a charge of 325 kg. of alkali cellulose ; the reaction is exothermic and usually takes two to four hours, according to the temperature, which should not be allowed to exceed 30° C. During churning the cream-coloured alkali cellulose gradually changes to yellow, orange-red and brown-red. Care has to be taken to stop churning before the cellulose xanthate commences to cake together in large masses, which is a sure indication of over-churning. An experienced operator can tell by the look of the material and by the rise in temperature when the churning has been carried far enough. At the end of the operation the excess of carbon bisulphide is either blown or sucked out, or it can be displaced by an inert gas, such as nitrogen or carbon dioxide (German Patent 375,712).

Production of Viscose.

Mixing.—The cellulose xanthate is next transferred from the churn to a vertical or horizontal mixer that consists simply of a cylindrical iron-jacketed vessel provided with a stirrer, which may be of various patterns (Figs. 5 and 6, facing p. 23). The cellulose xanthate is mixed in this vessel with sufficient soda and water to produce a viscose containing about 7–8% cellulose and 6·5–7% of alkali calculated as sodium hydroxide. The mixing may take three to six hours, and the solution is usually kept at 15°–17° C.† during this operation.

Ripening.—The viscose solution is sucked or blown from the mixer to tanks contained in a ripening-room or cellar at 15°–20° C.† The viscose, when freshly prepared, is not ready for spinning until a

* 325 kg. of alkali cellulose containing 26·5% cellulose theoretically requires 40 kg. of carbon bisulphide on the basis of 1 molecule $C_6H_{10}O_5$ to 1 molecule CS_2. The quantity generally used (30–32 kg.) corresponds approximately to 1·25–1·5 molecules $C_6H_{10}O_5$ to 1 molecule CS_2.

† See footnote on p. 19.

FIG. 5.—Vertical Viscose Mixer.
(*Dobson and Barlow, Ltd., Bolton.*)

[*To face p.* 22.

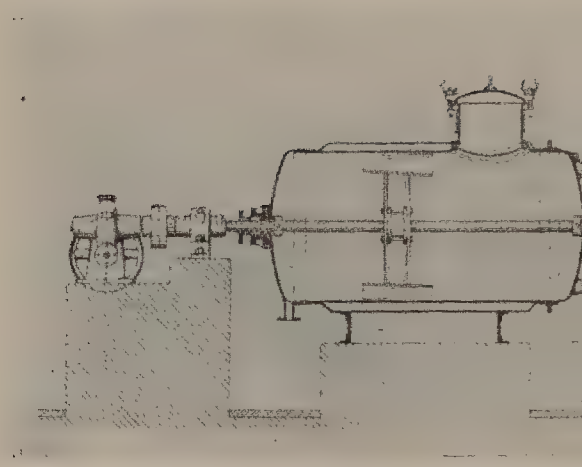


FIG. 6.—Horizontal Viscose Mixer.

(*John Hetherington & Son*

definite stage in the composition of the cellulose xanthate has been reached (see Chapter II.). A new viscose thus prepared may contain 2·25–2·5% sulphur, of which 1·6–1·8% sulphur is combined as cellulose xanthate, the rest of the sulphur being present in the form of sulphur by-products, such as sodium thiocarbonate. In a ripened viscose ready for spinning the content of sulphur combined as cellulose xanthate may have fallen to 1·1–0·9%. Cross has proposed expressing these values in terms of sodium (calculated as sodium hydroxide) combined with 100 parts of cellulose—this value being known as the cellulose-xanthate soda. For example, a content of 1·7% cellulose-xanthate sulphur in a viscose containing 7·5% cellulose corresponds to $\frac{1{\cdot}7 \times 40 \times 100}{64 \times 7{\cdot}5} = 14{\cdot}5\%$ cellulose-xanthate soda.

The determination of the cellulose-xanthate soda can be carried out quite simply in the laboratory. Rough determinations of the viscosity of the viscose are also made by observing the rate of fall of a steel ball between two marks through a sample of viscose contained in a glass tube. Other tests used for determining the degree of ripeness of the viscose are based on the salting-out effects of sodium or ammonium chlorides (see Appendix for details of carrying out such tests).

During the period of ripening, which usually takes about four to five days at 15°–20° C.* under the conditions and proportions given above for viscose production, the viscose has to be very carefully filtered to free it from fibres and any sediment which might choke up the spinning jets, and de-aerated.

The supply of suitable water is of great importance ; the presence of calcium salts from the water in the viscose is a frequent source of trouble in stopping up the spinning jets, owing to the difficulty in removing such salts by filtration.

* See footnote on p. 19.

Filtration.—Filtration is carried out by forcing the viscose from one tank to another by pressure and vacuum through filter presses. Three filtrations are usually necessary, through layers of cotton wool and finely-woven cotton fabrics; filtration is so arranged that the solution passes from the bottom to the top of the filter press to prevent air bubbles getting into it. A typical lay-out of viscose containers and filter presses, is shown in Fig. 7. The use of high-speed centrifugals for the filtration of cellulose solutions has been suggested, but does not appear to have been adopted to any extent except for the clarification of lacquers made from cellulose esters (*cf.*, English Patents 171,384 and 203,074).

De-aeration.—As soon as the viscose has been filtered it is stored in cylindrical vessels until required for supply to the spinning machine. It is kept under vacuum for at least twenty-four hours prior to spinning in order to eliminate all air bubbles, which would interfere with the spinning process.

The preparation of viscose as described in the preceding paragraphs is the normal process as carried out to-day in many factories. At the same time, it will be obvious that there is a possibility of many variations in the process in regard to the proportions of chemicals, the temperatures and times specified, and a study of the patent literature on viscose production fully bears this out.

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In the following recently published books will be found accounts of the viscose and other processes of manufacturing artificial silks :—

CLÉMENT ET RIVIÈRE. "Matières Plastiques Soies Artificielles," 1924.

FOLTZER. "Artificial Silk and its Manufacture," 1926.

A. CHAPLET. "Les Soies Artificielles," 1926.

HOTTENROTH. "Die Kunstseide," 1926.

SÜVERN. "Die kunstliche Seide" (Patent Compendium), 1926.

See also F. D. SNELL. *Chemistry and Industry*, 1926, **45**, 925.

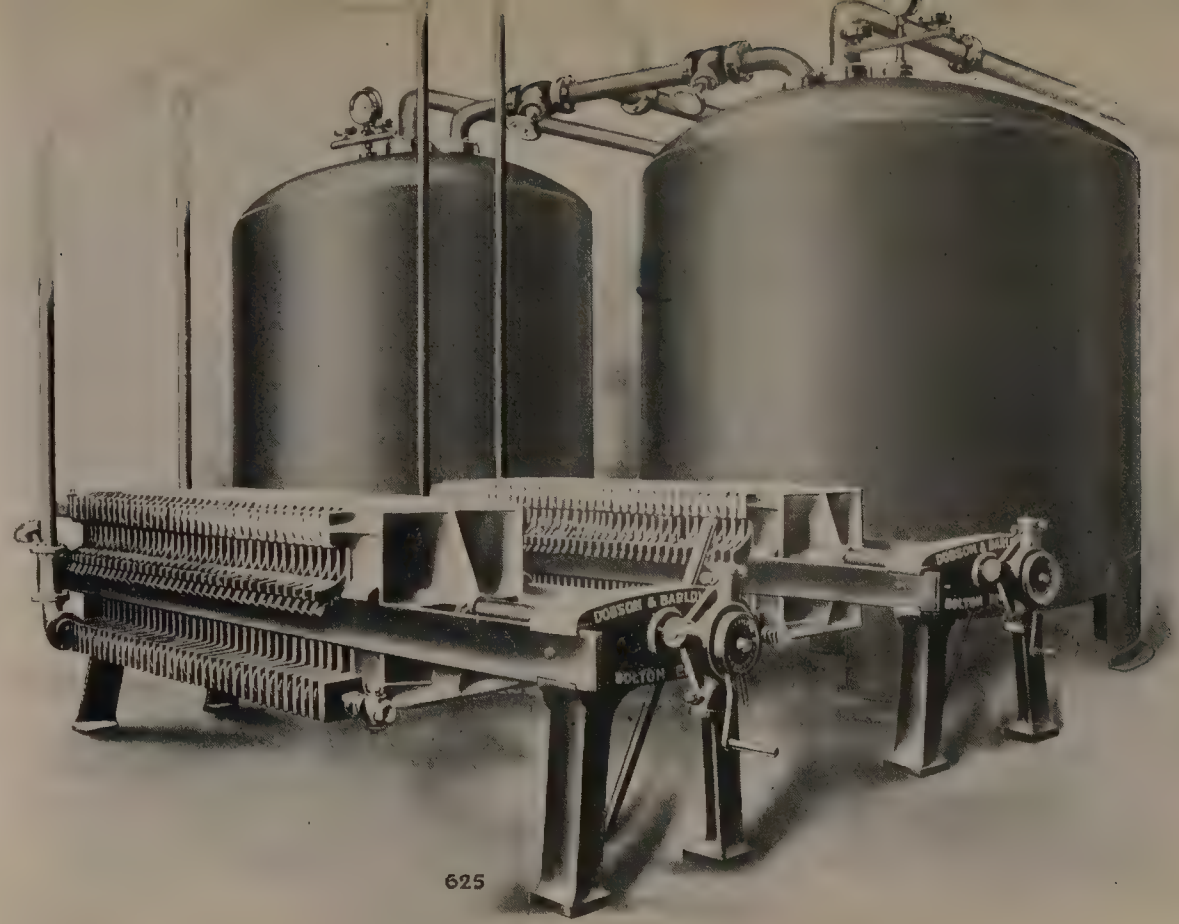


FIG. 7.—Viscose Containers and Filter Presses.

(*Dobson and Barlow, Ltd., Bolton.*)

[*To face p.* 24.

CHAPTER IV

VISCOSE PROCESS. II

2. Spinning

In the previous chapter the production of the viscose solution has been considered up to the point at which it is converted into artificial silk. Before dealing with the actual operation of spinning the viscose into a thread,* it is proposed to describe in some detail the machine by which this operation is carried out.

There are two types of spinning machine used in viscose manufacture :—

(*a*) The centrifugal box (pot or can) spinning machine.
(*b*) The bobbin spinning machine.

In the former machine the thread, comprising several filaments, is fed vertically into a metal box revolving at a very high speed (centrifugal), and thereby receives a twist, being coiled round the inside of the receiver by the centrifugal force. In the latter machine the composite thread is collected untwisted on bobbins, and has to be subsequently twisted on a special machine. Each type has its advantages and disadvantages, but the centrifugal machine is gradually displacing the other for the production of most sizes of yarn.

(a) Centrifugal Box-Spinning Machine.

The principle on which this machine is based is not new, and has been applied for other purposes in connection with textiles, though Topham was the first

* By a thread is meant the composite thread produced by collecting together a number of filaments. A thread of artificial silk is usually measured in deniers, the denier being taken as the weight in milligrams of 9 metres (Italian or legal system).

to patent its application to artificial-thread production (English Patent 23,158 of 1900).

A diagrammatic illustration of the centrifugal spinning in its simplest form is shown in Fig. 8. A thread is formed in the bath at the jet J and carried over a rotating pulley or godet at P ; it descends the funnel

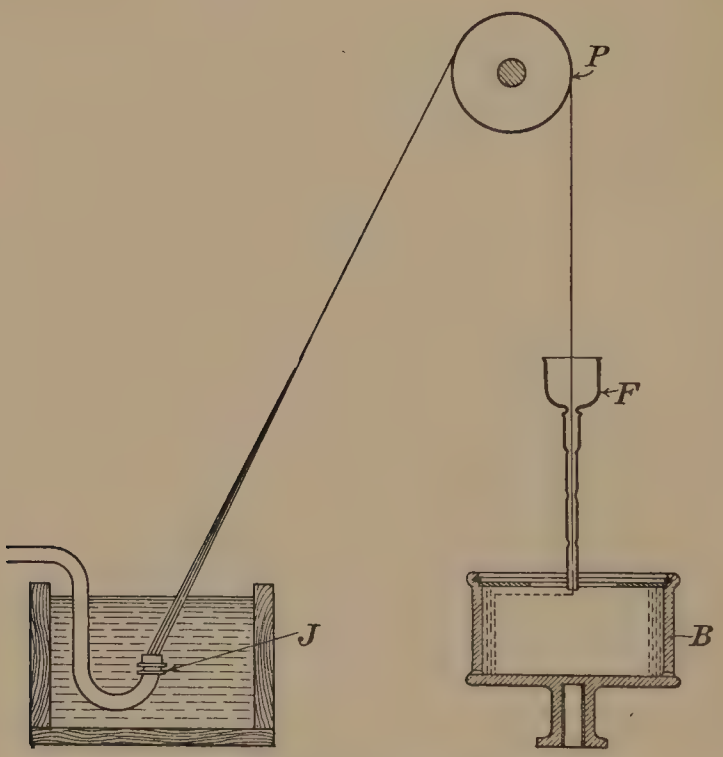


FIG. 8.—Diagram of Centrifugal Spinning.

F, and leaves it at an angle of 90°, being twisted and coiled in the swiftly-rotating box B.

If the peripheral speed of the pulley drawing off the thread (spinning speed) is 50 metres per minute, and the speed of the rotating box is 5,000 r.p.m., the twist produced in the thread should be $\frac{5{,}000}{50} = 100$ turns per metre, or 2·54 turns per inch, of thread spun.

The following tables give the theoretical twist produced for a series of spinning (Table I) and box speeds (Table II) :—

TABLE I

Spinning speed in metres per minute	Box-speed 5,000 revolutions per minute. Twist in turns	
	per metre	per inch
45	111	2·79
50	100	2·54
55	91	2·31
60	83	2·10
65	77	1·95
70	71	1·80
75	67	1·70
80	63	1·60

TABLE II

Spinning speed 60 metres per minute. Box-revolutions per minute	Twist in turns	
	per metre	per inch
2,000	33	0·84
3,000	50	1·27
4,000	67	1·70
5,000	83	2·10
6,000	100	2·54
7,000	117	3·04
8,000	133	3·37
9,000	150	3·80
10,000	167	4·24

It should, however, be pointed out that these theoretical twists are not always obtained, owing to slip of the thread on the pulley. In practice the spinning speed and the box-speeds are so adjusted that the twist averages 2–2·5 turns per inch. Recent tendency has been to increase spinning speed so as to increase the output per spindle.

The principal parts of the spinning machine from the point of view of accurate spinning are as follows :—

Pump.
Candle filter.
Jet.
Godet.
Funnel.
Spinning box.

These parts will first be considered in detail before the spinning machine is described as a working unit.

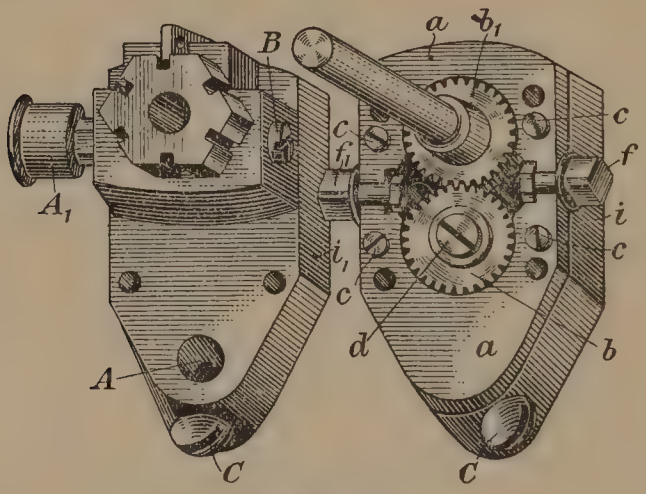


FIG. 9.—Gear-wheel Pump.
(*Arendt and Weicher, Berlin.*)

Pump.—The spinning pump constitutes one of the most important parts of the spinning machine, because on its accurate working depends the correctness in denier and uniformity of the spun thread.

Two types of pump are in use :—

(i) Gear-wheel pump.
(ii) Piston pump.

(i) *Gear-wheel Pump.*—The gear-wheel pump (1), as its name implies, consists of two accurately-cut intermeshing gear wheels, which pump the solution as the wheels rotate. In the most improved designs (see Fig. 9) provision is made for the adjustment of the

gear-wheels. The great advantages of this pump are :—

(*a*) Simplicity of construction.
(*b*) Facility with which it can be cleaned.
(*c*) Cheapness.
(*d*) Positiveness of drive.
(*e*) Evenness of delivery, so that an air bottle is not required.

On the other hand, the gear-wheels soon become worn, and unevenness in output results.

In the pump illustrated, which shows on the right hand a view of the inner plate of the pump and gear-wheels, and on the left the back outer cover, the positions of the pinions *bb'* are radially adjustable to each other, and the inner plate *aa* is also adjustable to the circumference of each pinion by means of the screws *cc*. The viscose enters at A and leaves at the corresponding hole on the other side of the pump ; the pump is held in a suitable hollow bracket, and can be thrown in or out of action by swivelling about these outlet and inlet holes. The variation in delivery of such pumps is $\pm$ 2%, but this may be considerably exceeded unless the pump delivery is carefully tested from time to time and adjustments made to allow for wear of the gear-wheels (2).

(ii) *Piston or Plunger Pump*.—The first piston pump for artificial-silk spinning was patented by Stearn in 1903, and consisted of a single-plunger pump with inlet and outlet valves (3). In order to prevent inequalities in pressure between the successive strokes of the plunger, an air bottle was connected to the outlet side. The most successful of this class of pump is the Clayton pump (4), in which two or four plungers *25*, *26*, operating against a cam *41*, work in the cavities or cylinders *20*, *21* of a rotating cylinder *7*. The stroke of each piston is so arranged that the suction or compression stroke occurs at the moment the openings in the internal rotating cylinder are opposite the inlet *13* or

outlet *14* openings of the outer casing *9*. The stroke of the pumps can be varied (by 5–10%) by adjusting the position of the cam (see Figs. 10A, 10B, 10C). An air chamber *36* is nearly always necessary with this

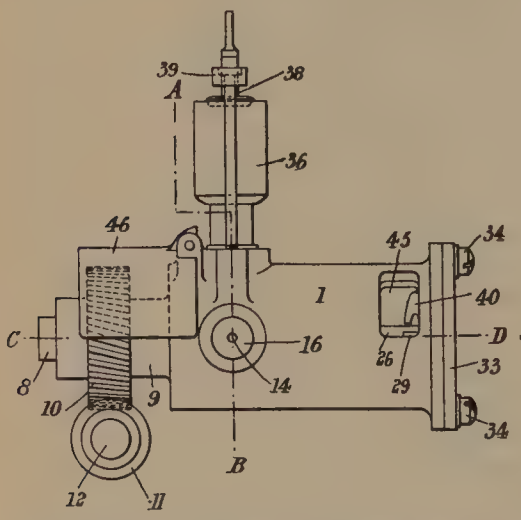


FIG. 10A.—Elevation of Clayton Pump, showing Method of Drive and Air Bottle.
(*English Patent* 17,876 *of* 1907.)

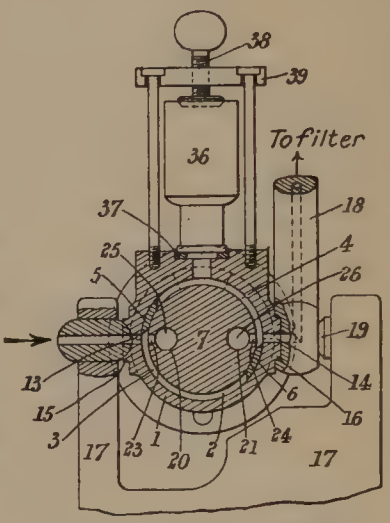


FIG. 10B.—End View and Section of Clayton Pump, showing Method of fixing Pump in Bracket.
(*English Patent* 17,876 *of* 1907.)

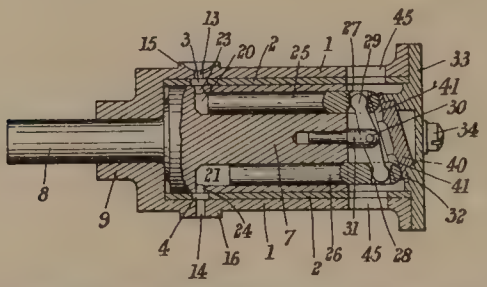


FIG. 10C.—Longitudinal Section through Clayton Pump, showing Pistons and Cam.
(*English Patent* 17,876 *of* 1907.)

type of pump. Recent improvements in the design of pumps of this class are concerned chiefly with an increase in the number of pistons, which may be two, three, five, six or nine, though usually three, six or nine are used (5).

A modern pump of similar design, but having two

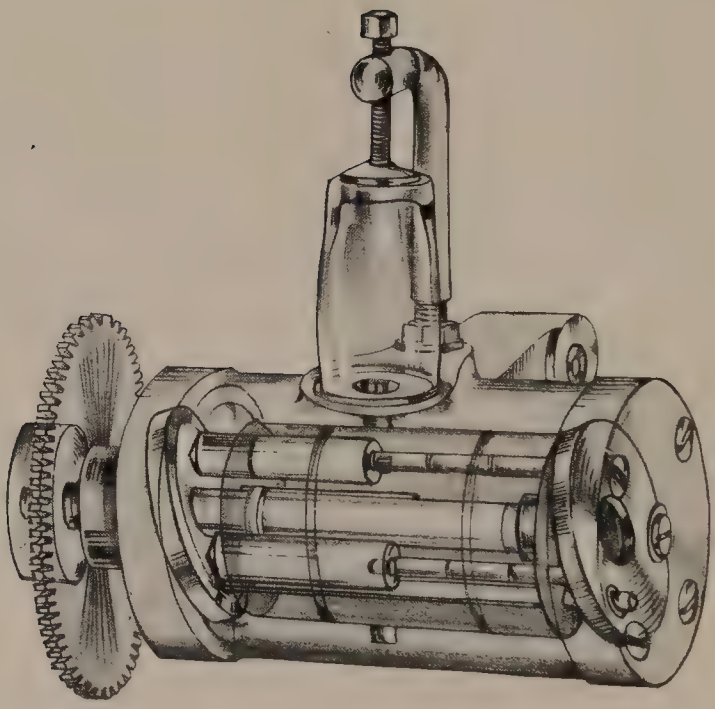


FIG. 11.—Borletti Spinning Pump.

(*Horology, Ltd., London.*)

[*To face p.* 31.

cams and three pistons, is shown in Fig. 11. The manufacturers of this pump, which is widely used, claim an accuracy of output, when set, of ± 1% approximately, and a variation in the output of one pump to another of 2·5%.

The piston pumps are certainly more accurate, and

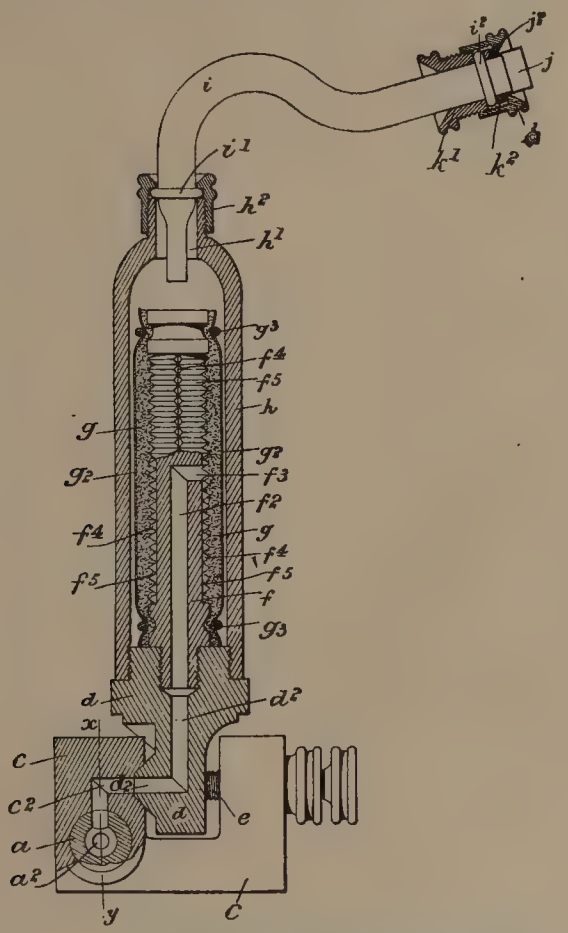


FIG. 12.—Sectional Elevation of Ebonite Filter.
(*English Patent* 23,157 *of* 1900.)

maintain their accuracy for longer periods than the gear-wheel pumps. On the other hand, they are more complicated, and consequently cost more to manufacture. The air vessel has also been a source of trouble owing to the top surface of the viscose becoming stagnant and coagulating in the air vessel, which then fails to function properly and may fracture. In the latest

design this disadvantage has been overcome by arranging the circulation of the viscose so that the viscose in the bottle is constantly being renewed.

Candle Filter.—Although the viscose supplied to the spinning machine has undergone several filtrations (see Chapter III.), yet it is found necessary to subject it to a final filtration on the spinning machine before it reaches the jet. The original design patented by Topham in 1900 (6) has been very widely adopted, and is used in most viscose factories to this day. It consists of an outer ebonite casing *h* (see Figs. 12 and 13) and an inner serrated candle *f* of the same material covered with fine filtering material, such as nainsook or cambric. The filter is fixed in a bracket *c*, and can be swivelled about the cone joint as shown in the illustra-

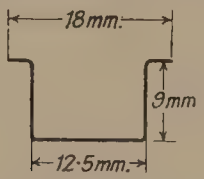
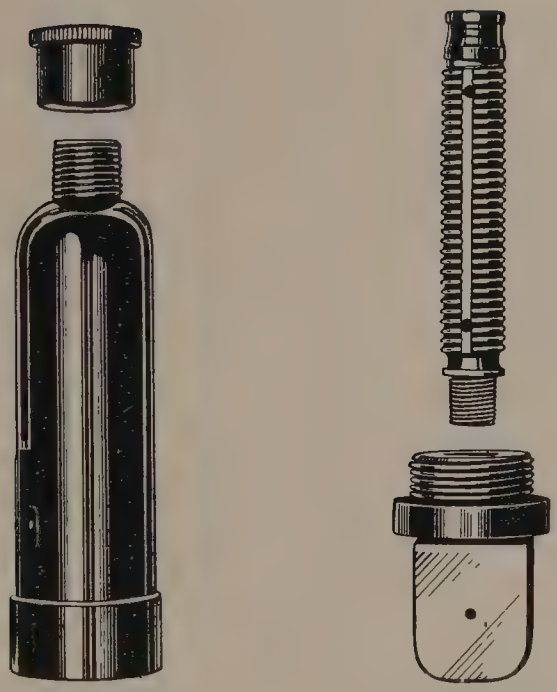


FIG. 14A.—Typical Dimensions of Spinning Jet with 18–50 holes.

FIG. 14B.—View of Jet.

tion. The viscose enters the filter at the bottom and is forced up through the centre of the candle, passing out through the filtering material, at holes suitably spaced in the candle, into the annular space between the candle and casing, and so on to the jet. Dreaper has patented a modification of this filter (7) in which the viscose flows direct into the outer casing and then passes out through the candle to the jet.

Jet.—The jets in viscose-spinning may be made of glass or metal (porcelain has been suggested), and consist usually of a small cylinder which is closed at one end and has a flange at the other for connecting up to the supply of spinning solution (see Fig. 14A, 14B). The closed end of the cylinder is perforated with a number of evenly-spaced and accurately-drilled holes, the number and diameter of which depend on the denier of thread it is desired to spin.



Outer Casing. Inner Candle.

FIG. 13.—Ebonite Filter.

(*C. Macintosh & Co., Ltd., Manchester.*)

[*To face p.* 32.

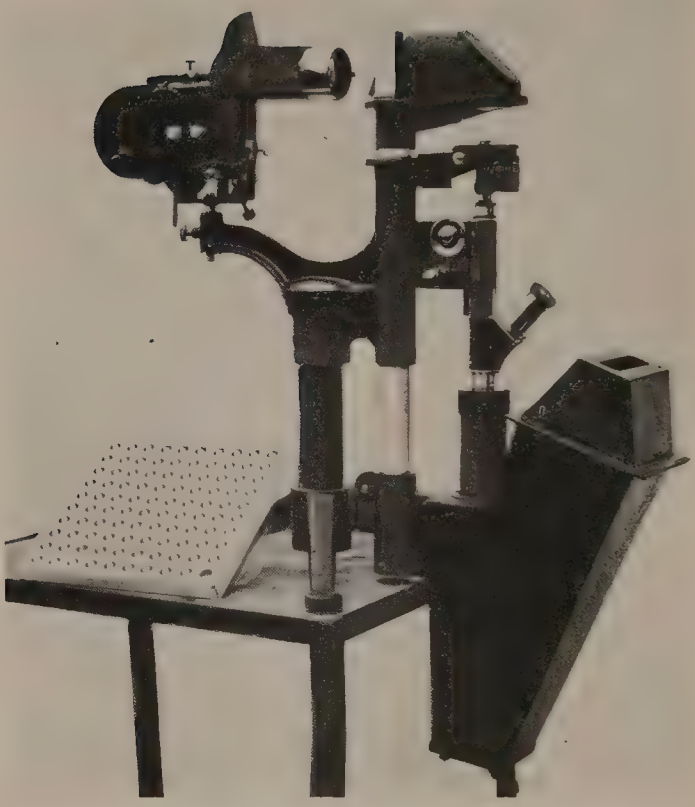


FIG. 15.—Apparatus for the Examination and Measurement of Spinning Jet Holes.

(*Leitz and Heraeus.*)

[*To face p.* 33.

Glass jets are produced by sealing in fine metal wires and dissolving them out chemically. Metal jets, however, are generally employed; they are made of acid-resisting metals or alloys, such as platinum, platinum-iridium, gold-platinum (80–90% gold), and gold-palladium * (8). The sizes of the holes for ordinary deniers (150–250) may range from 0·05–0·1 mm., and such holes can be drilled with an accuracy of ± 0·002 mm. The number of holes per jet will depend on the denier and fineness of the filaments of the thread required. Thus the present tendency in artificial-silk manufacture is to produce composite threads containing as many individual filaments as possible to a given size of thread. Some years ago 6–8 deniers per filament, *i.e.*, 24–18 filaments (or holes per jet) for a 150-denier thread, was considered suitable, but with the improvements in spinning methods 50–36 filaments (or holes per jet) for such a thread is not uncommon, *i.e.*, 3–4 deniers per filament (9). There are a large number of patents covering variations of the type of jet described; they range from methods of making composite jets, so as to economise the amount of rare metal used in their construction, to varying the design of the jet, so as to ensure rapid coagulation of the issuing viscose or other cellulose solution (10, 11).

The checking and examination of the diameters of the jet holes is a matter of considerable importance if uniform filaments are to be produced. An apparatus for the rapid examination and measurement of the holes in spinning jets has lately been put on the market by two German firms (see Fig. 15). In this apparatus the picture of the hole, magnified 130–150 diameters, is thrown on to a ground-glass plate. Any irregularities or undue wear in a hole can then be easily seen, and the diameter can be readily measured and checked against a standard (12).

* The typical dimensions of a jet used for spinning medium deniers are given in Fig. 14A.

Glass Hook, Godet, and Funnel.—In order to guide the thread (formed from the viscose extruded into the spinning bath) to the centrifugal spinning box, glass devices are generally used as guides, viz., the hook, the godet, and the funnel :—

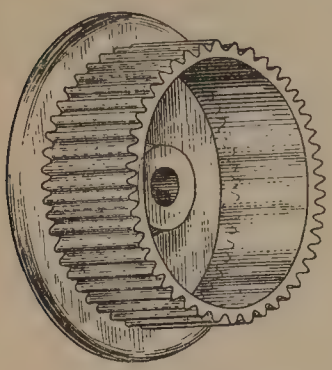


Fig. 16.—Godet Roller.

(*a*) *Hook.*—This usually consists of a piece of glass rod bent in form of a round hook, under which the thread passes on emergence from the spinning bath. By altering its distance from the jet the length of immersion of the thread in the bath can be varied.

(*b*) *Godet Roller.*—In order to carry the thread forward to the funnel and spinning box, it passes up from the hook over a glass pulley or roller (known as a godet roller, or simply godet). The peripheral speed of the godet determines within limits the spinning speed, *i.e.*, the rate at which the thread is drawn away from the jet. There is, however, a slight slip on the godet, caused by the pull on the thread by the spinning box. In the so-called stretch spinning process (see p. 40), in which tension is put on the thread before it reaches the godet so as to draw out the thread, the slip on the godet is, of course, greater. This godet is usually made of ebonite or glass and may have either a plain surface or serrations, forming a sort of gear-wheel with smoothed teeth (Fig. 16).

Fig. 17.— Spinning Funnel. (*English Patent* 104,225.)

(*c*) *Funnel.*—In order to guide the thread from the godet vertically into the centrifugal spinning box, a funnel with a long stem is used. This funnel is nearly always made of glass, and is generally

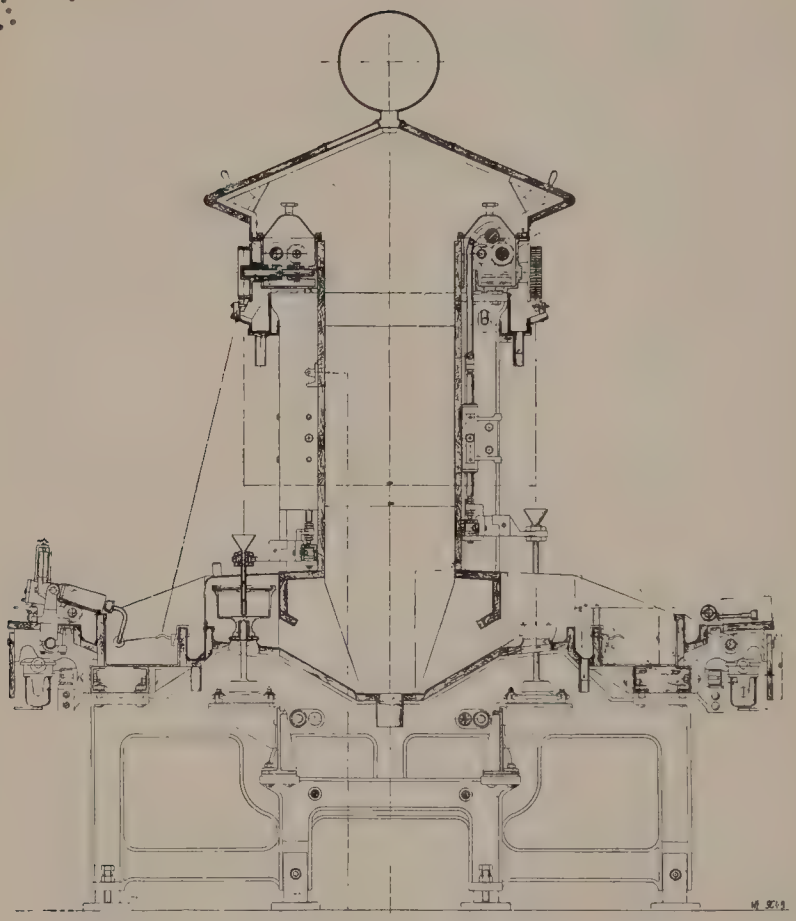


FIG. 19B.—Side Elevation of Centrifugal Spinning Machine.

(*John Hetherington & Sons, Ltd., Manchester.*)

[*To face p.* 35.

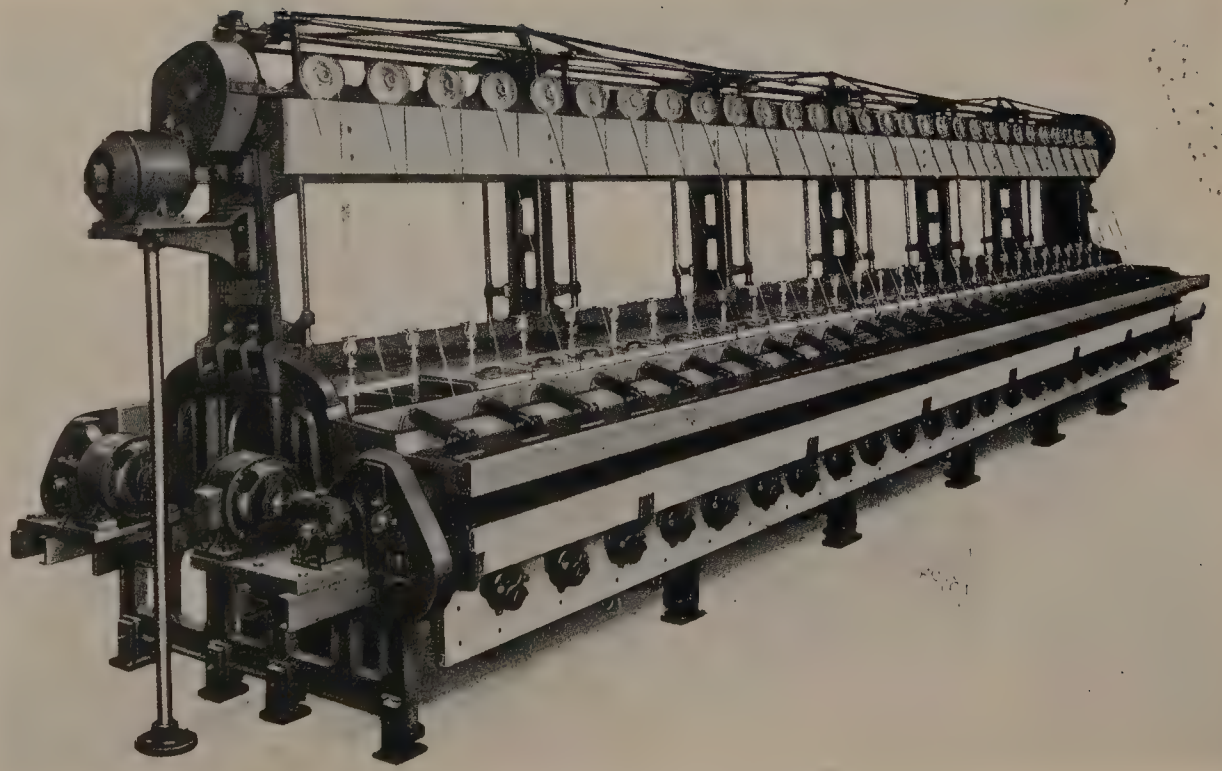


FIG. 20.—Centrifugal Spinning Machine.

(Haubold, of Chemnitz.)

[*To face p.* 35.

shaped with constrictions in the tube (Fig. 17). The funnel illustrated is fitted with a special collar for correct centering (13).

Spinning Box.—The centrifugal spinning box, in which the thread is coiled and twisted, is usually made of aluminium and lined with ebonite, and is provided with small holes for the exit of the excess liquid carried over by the thread (14). The base of the box is provided with a foot, which fits on to the spindle by which the box is rotated. A typical type of box is shown in Fig. 18A. The box is provided with a lid, kept in place

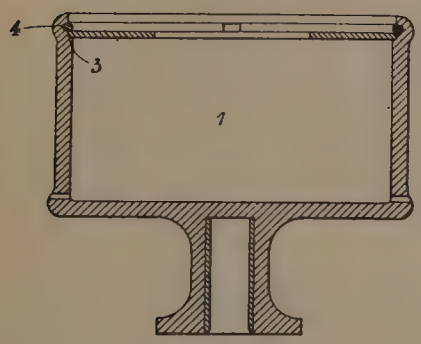


FIG. 18A.—Sectional Elevation of Spinning Box.
(*English Patent* 25,097 *of* 1908.)

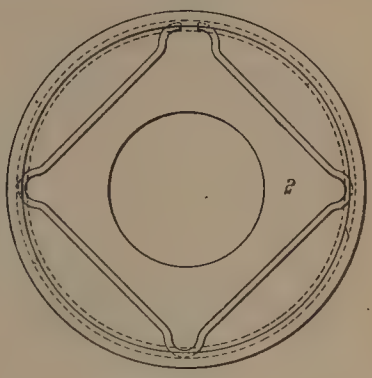


FIG. 18B.—Plan of Spinning Box showing Method of fixing Lid by a Spring.
(*English Patent* 25,097 *of* 1908).

by a wire spring (Fig. 18B). These boxes have to be very carefully balanced so that they run true at the high speeds required.

The foregoing description of the chief component parts of the centrifugal spinning machine now enables the actual process of spinning to be described. Typical spinning machines are shown in section in Figs. 19A and 19B, and typical photographs of modern machines will be seen in Figs. 20A and 21B, facing p. 36. The machine illustrated in Fig. 20 has thirty jets to one side of the machine.

From Fig. 19 it will be seen that the viscose is fed

to the pump (P), and then passes through the candle filter (F) by a glass tube to the jet (J), held in a suitable holder. The thread formed by coagulation of the viscose in the spinning bath (B) passes under the hook (H) to the godet (G), down the funnel (L), into the spinning box (S), where it is coiled up evenly in the form of a hollow cake of thread (see Fig. 23).

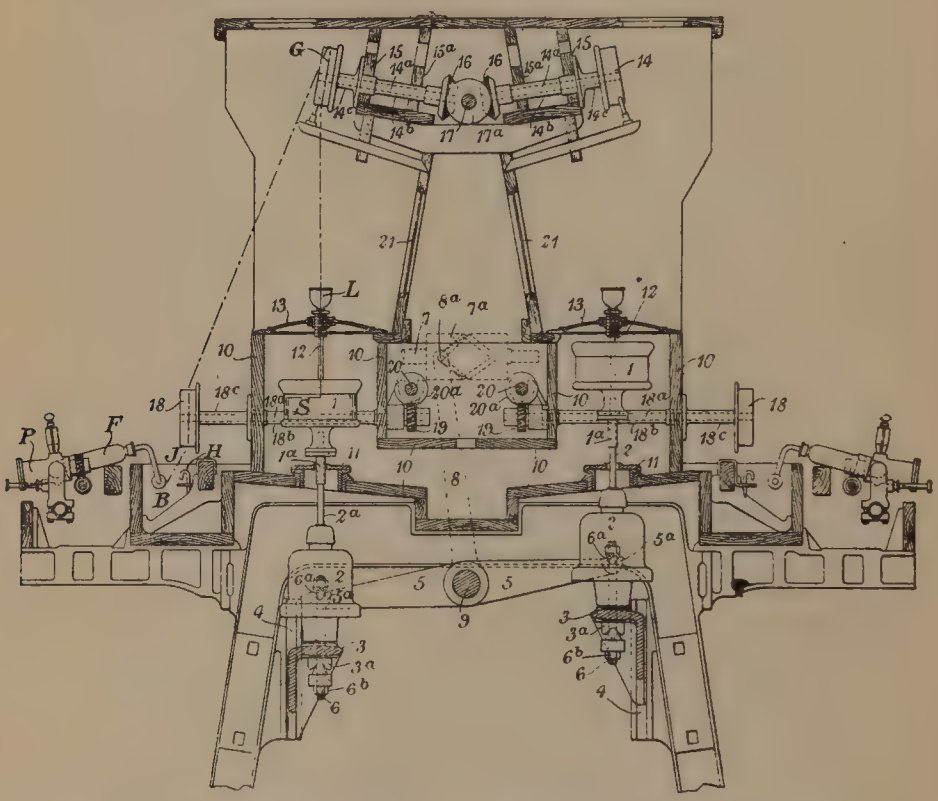


FIG. 19A.—Sectional Elevation of Centrifugal Spinning Machine.
(*English Patent* 104,363.)

This is accomplished by the up-and-down traverse of the funnel (ten to thirty per minute), but can also be effected by an up-and-down motion of the spinning box (as shown in Fig. 19A). The weight of wet thread which can be collected in the size of box usually adopted is about 1 lb.; the time taken for this amount to be collected will depend on the denier of the thread and spinning speed. The spinning box may be driven

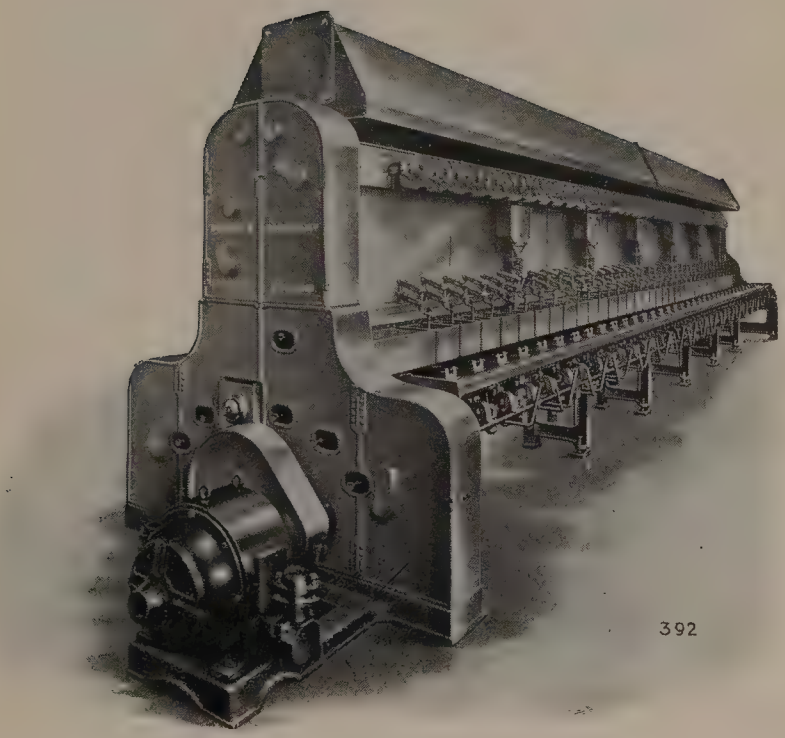


FIG. 21A.—Centrifugal Spinning Machine.

(*Dobson and Barlow, Ltd., Bolton.*)

[*To face p.* 36.

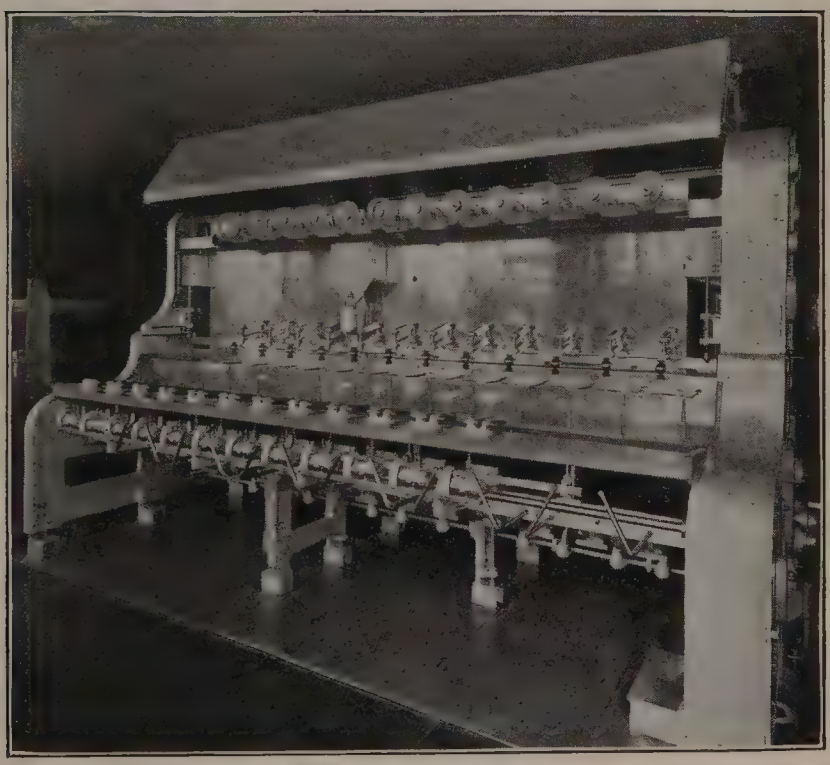


FIG. 21B.—Centrifugal Spinning Machine.

(Dobson and Barlow, Ltd., Bolton.)

[*To face p.* 36.

by worm-wheel, roller chain, friction drive or individual motors. The last method is gradually displacing other methods, as it is more reliable and enables a wide range of centrifugal speeds to be obtained by electrical methods of speed control (variation of frequencies).

It is not proposed to deal here with the very large

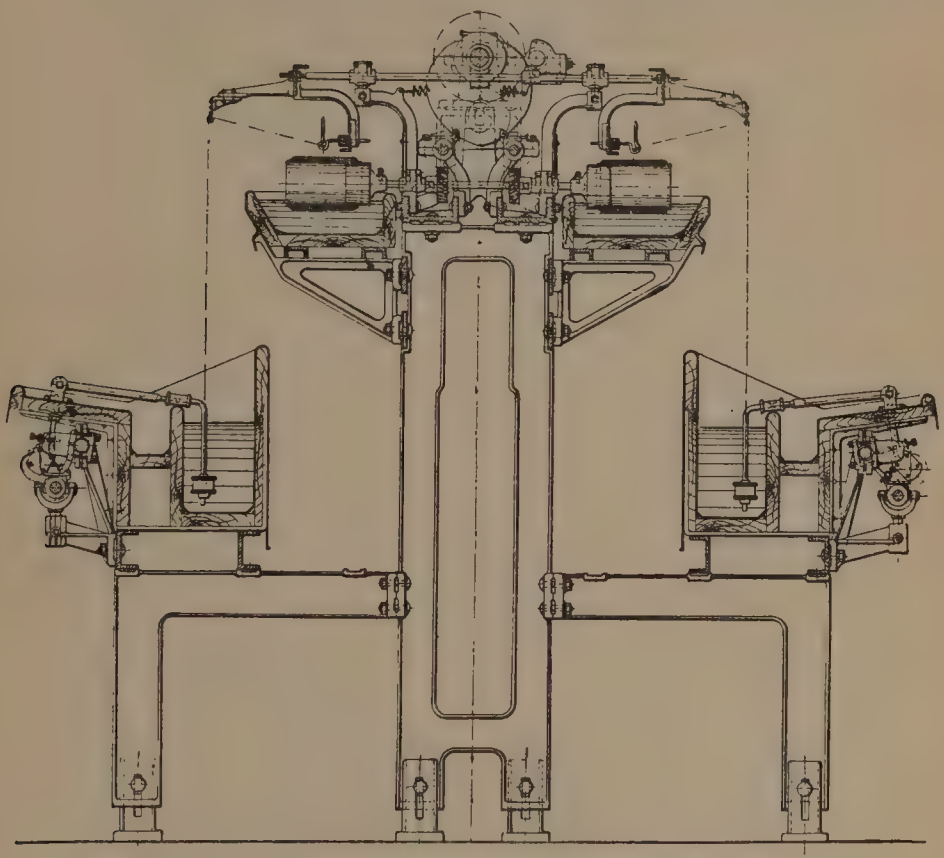


FIG. 22.—Sectional Elevation of Bobbin Spinning Machine.
(*Carl Hamel, of Chemnitz.*)

numbers of different types of machine and methods of drive, but the general lay-out of centrifugal spinning machines and their method of operation are necessarily similar in many respects.

(b) Bobbin Spinning Machine.

In a bobbin spinning machine the pump, filter and

jet are the same as in the centrifugal spinning machine ; the filaments from the jet, however, are passed through a guide with a reciprocal motion, so that the thread is cross-wound on the collecting bobbin. The bobbin is made of glass, aluminium, or wood (see Fig. 22).

The collecting bobbin may rotate in a dilute setting bath. Most bobbin spinning machines are provided with ingenious mechanical devices for changing over from a full to an empty bobbin without interrupting the spinning. The spinning speed depends on the peripheral speed of the collecting bobbin, which is generally less than the spinning speed in the centrifugal spinning machine ; a typical speed is about 45 metres per minute.

The threads produced by the bobbin spinning and centrifugal-spinning methods differ somewhat in properties, the former producing a smoother, more even, and more compact thread than the latter. Moreover, there is more chance of unevenness in the bobbin-spun threads, owing to the increase in periphery of the bobbin, although this is compensated for by mechanical means. It has been stated that bobbin spinning is better for the finer deniers (below eighty denier), whilst the centrifugal spinning is preferable for the higher deniers (15).

Spinning Bath.

So far no mention has been made of the spinning bath, by which the viscose is converted into the cellulose threads. In the original process it was proposed to convert the sodium-cellulose xanthate into the insoluble ammonium salt, and then to decompose this compound in a second bath by acid. This method was soon superseded by the combined bath of acid and salt or acid salts, generally sulphuric acid and sodium sulphate together with ammonium and/or other sulphate. Further research showed that the addition of organic compounds, *e.g.*, carbohydrates,

was an advantage in keeping the spun thread moist and preventing the crystallisation of the salts which were objectionable in reeling, and in generally improving the quality of the thread, such as its strength and covering power.

The following compositions of spinning baths that have been patented are typical of those used in general practice at the present day :—

(*a*) *Muller Bath.* English Patent 10,094/1906.

Sodium bisulphate	40 kg.
Water	60 „
Sulphuric acid (66%)	7 „

(*b*) *Courtaulds and Wilson.* English Patent 21,405/1907.

Sulphuric acid	10%
Glucose	30%
Water and sodium sulphate	60%

(*c*) *Courtaulds and Wilson.* English Patent 5,595/1908.

Sulphuric acid	8%
Ammonium sulphate	17·5%
Glucose	7·5%
Water and sodium sulphate	67%

(*d*) *Courtaulds and Napper.* English Patent 406/1911.

Sulphuric acid	8%
Glucose	10%
Sodium sulphate	12%
Zinc sulphate	1%
Water	69%

The number of different spinning baths patented is very large, and patentees have made very wide claims for the special properties conferred on the thread produced by the special bath or baths specified in their patents. In some cases the addition of certain inorganic or organic compounds to the viscose has been patented as a method by which the said compounds can be introduced into the spinning bath.

It must also be borne in mind that there are three * other factors which, in conjunction with the composition of the spinning bath, can be varied and which may affect the thread produced. These are the temperature of the spinning bath, the length of immersion of the thread, *i.e.*, from the jet to the hook, and the rate of spinning. The optimum temperature for spinning is usually considered to be between 35° and 45° C., immersion may vary between 2·5 and 25 cm., whilst the rate of spinning may vary between 40 and 60 meters per min. (see p. 27); but the practice of different factories varies considerably in these respects.

Attention has in recent years been directed to the so-called stretch-spinning process (see also p. 56). This was originally adopted for cuprammonium spinning, as it enabled a very fine thread to be drawn out from a comparatively thick one during the operation of spinning by using a very slow-setting spinning bath. The demand for fine threads turned the attention of inventors to applying this process to viscose spinning. It was found that a certain tension could be put on the thread during spinning, thereby increasing its strength, but reducing its elasticity. (The provision of the extra godet shown in Fig. 19 is for this purpose.) Bronnert (16) has studied the conditions necessary for the production of very fine viscose threads, and has incorporated his results in a large number of patents. He claims broadly that the producing of fine filaments is a function of the acid concentration in the spinning bath; and he has worked out a number of relationships between degree of ripeness of the viscose, viscosity of and additions to the viscose, composition and concentration of the spinning bath, temperature and acidity of the spinning bath, nature of additions thereto, size of holes in jet, spinning speed, and the drawing out of the thread. He states that for any given viscose and jet-

* The state of ripeness of the viscose is also an important factor; but this has already been referred to on p. 22.

hole diameter there must be a minimum concentration of acid present in the spinning bath, which is said to vary inversely as the square of the denier of thread spun. The acid concentration should be higher the finer the threads are to be drawn out. The whole series of patents represents a very important study of the conditions necessary to produce fine filaments from viscose. Bronnert claims to have produced threads down to 0·75 filaments per denier by his methods.

References.

(1) KUTTNER. English Patent 28,320 of 1912.
(2) E. WURTZ. *Chemische Apparatur*, 1926, **13**, 237.
H. JENTGEN. *Die Kunstseide*, 1925, **7**, 49.
(3) STEARN. English Patent 16,605 of 1903.
(4) CLAYTON. English Patent 17,876 of 1907.
(5) GEBEREICH. *Die Kunstseide*, 1925, **7**, 97.
(6) TOPHAM. English Patent 23,157 of 1900.
(7) DREAPER. English Patent 207,214.
(8) DREAPER. English Patent 260,672.
(9) TAYLOR. *Manchester Guardian Artificial Silk Supplement*, April 15, 1926.
(10) KUHNET. German Patent 360,000.
CRIGGALL. English Patent 18,965 of 1912.
(11) KÖLN-ROTTWEIL. German Patent 319,443 of 1919.
SCHRODER. German Patent 395,524 of 1922.
HARTOGS. German Patent 403,735 of 1922.
(12) *Die Kunstseide*, 1926, **8**, 424.
(13) COURTAULDS and CLAYTON. English Patent 104,225.
(14) COURTAULDS and CLAYTON. English Patent 25,097 of 1908.
(15) LEHNER. *Manchester Guardian Artificial Silk Supplement*, April 15, 1926.
(16) BRONNERT. English Patents 163,817, 163,466, 166,931, 169,190, 170,024, 170,029, 170,322, 170,874, 171,125, 172,038, 174,960, 174,961, 190,772, 192,214; *J. Soc. Dyers and Colorists*, 1922, **38**, 153.

CHAPTER V

VISCOSE PROCESS. III

3. Finishing

In the last chapter the spinning of artificial silk by the centrifugal and bobbin spinning machines was followed up to the production of " cakes " or bobbins of thread ; the further stages through which the spun thread passes before the finished artificial silk is obtained will now be described. The scheme of operations can be followed from the flow-sheet, which shows the after-treatment of the spun thread from both types of machine up to the production of the finished yarn as unbleached or bleached artificial silk :—

" Cakes " from the Centrifugal Spinning Machine.

The thread from the centrifugal machines generally has a twist of approximately 2·5 turns per inch (see p. 27). The cake of thread can, therefore, be reeled or wound direct into skeins or hanks. To prevent, however, any drying off of the cakes prior to the reeling process, which would increase the difficulties of reeling, special humidifying chambers are provided for the storing of the cakes (1).

Reeling and Lacing.—The operation of reeling, which consists simply in winding off a definite length of thread into a skein or hank, has to be carried out with considerable care, as the thread in the wet state and before the first drying is very tender.

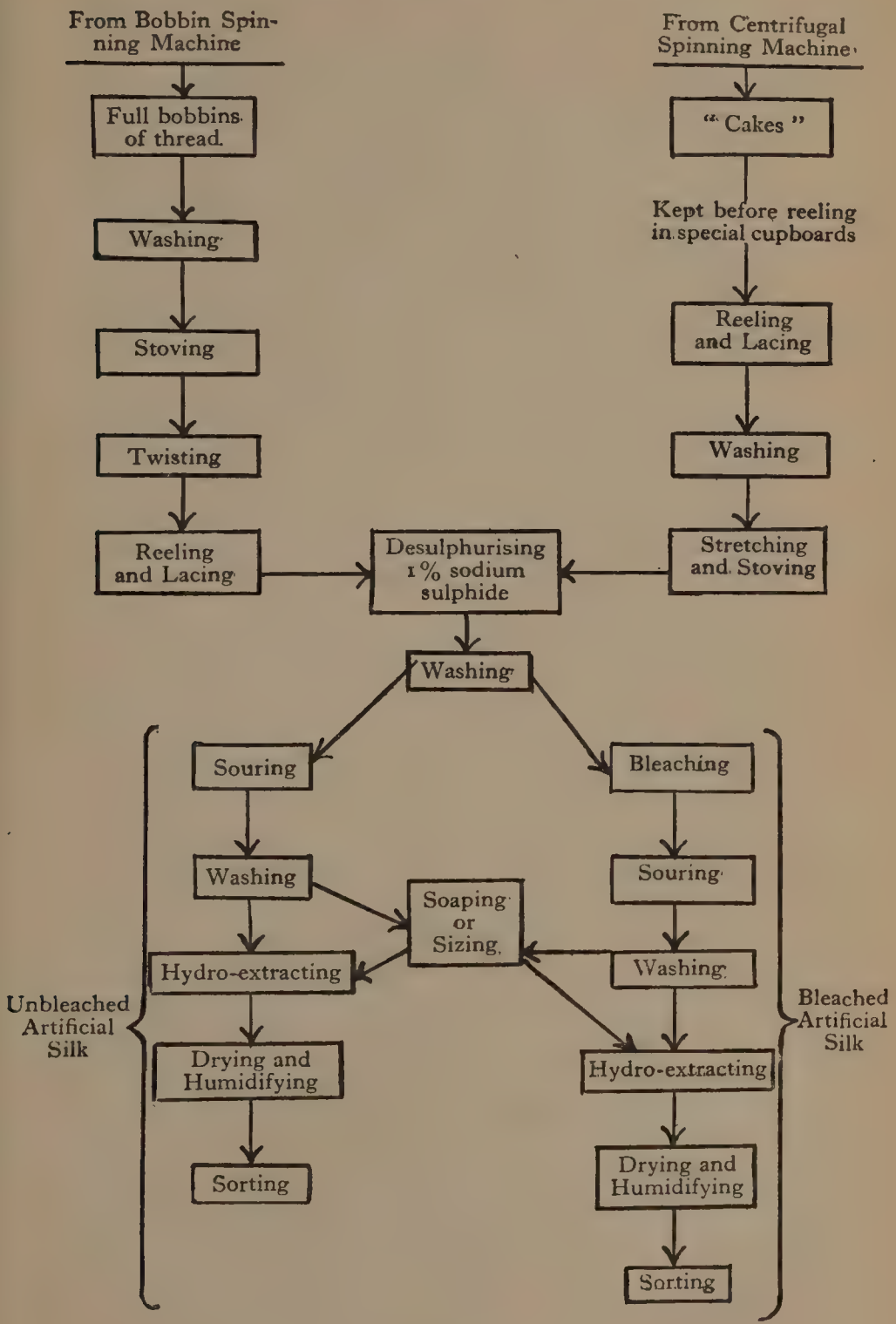
A typical reeling machine is shown in Fig. 23, which enables twenty cakes to be reeled into skeins simultaneously. The wooden frame or " swift," as it is called, on which the hank is wound is self-contained and has its own separate traverse and stop motion, so

FIG. 23.—Reeling Machine.

(Joseph Stubbs, Ltd. Manchester.)

To face p. 42.

Flow-Sheet for Viscose Process II.



that if the thread from one of the cakes breaks suddenly the reeling of that particular swift stops automatically. The speed of reeling is usually about 300 r.p.m. All parts likely to come in contact with the thread must be made of wood or acid-resisting metal. The swifts are usually capable of adjustment to any given circumference, and also have a releasing arrangement, so that the reeled skein can be freed easily from the swift without rubbing. The circumference of the swift is generally 44 inches, and skeins may be reeled in lengths of 1,680 or 3,360 yards, or, if the metric system is used, the circumference of the reel is 1,100 mm., and lengths of 1,500 or 3,000 metres are reeled, according to the denier. In most types of machines, the traverse motion for the thread on each swift produces clear, open diamonds through which the lacing thread can be inserted.

Four cross-lacings of silk, cotton or artificial silk are inserted in each skein to keep the skein in order through the subsequent operations. The ends of the skein are as a rule tied to the same lacing. The lacings may be dyed to act as distinguishing marks for different deniers or for other purposes ; the dyes used must however, be fast to the chemicals used in the processes through which the silk has subsequently to pass.

Washing.—The reeled skeins are now placed on smooth ebonite or glass rods and thoroughly washed free of all traces of acid and salts derived from the spinning bath.

Formerly this was carried out by passing the skeins through a series of vats containing water, but this method of washing, which involved a considerable amount of handling, is now generally carried out by means of automatic washing machines, whereby the skeins, depending from rods, are automatically carried forward by friction rollers. A machine working on this principle was patented by Clayton in 1913 (2). End and side elevations of the machine are shown in Figs. 24A and 24B. The skeins placed on rods *28* are

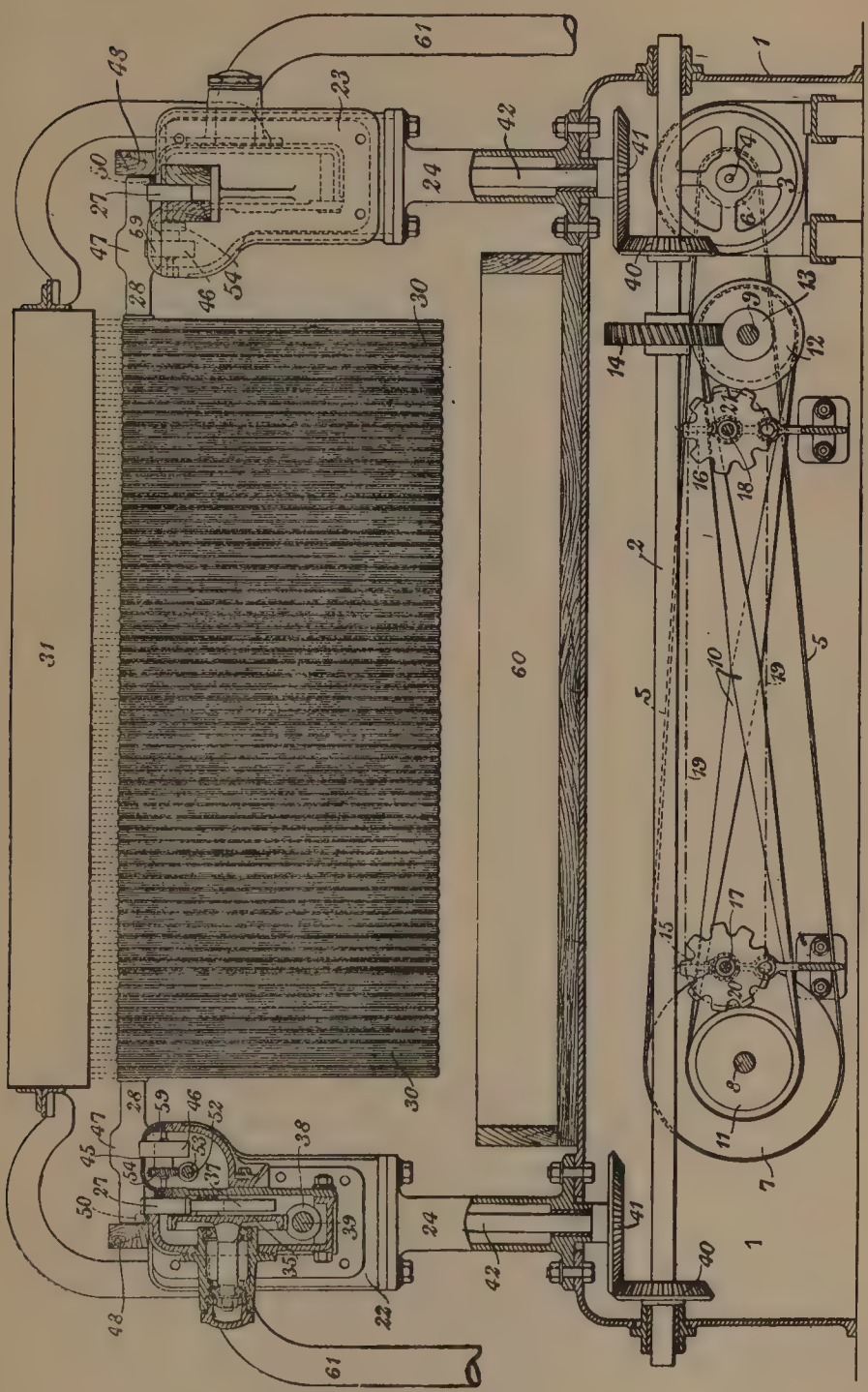


FIG 24A.—Sectional Elevation of Skein-washing Machine.
(*English Patent* 9,067 *of* 1913.)

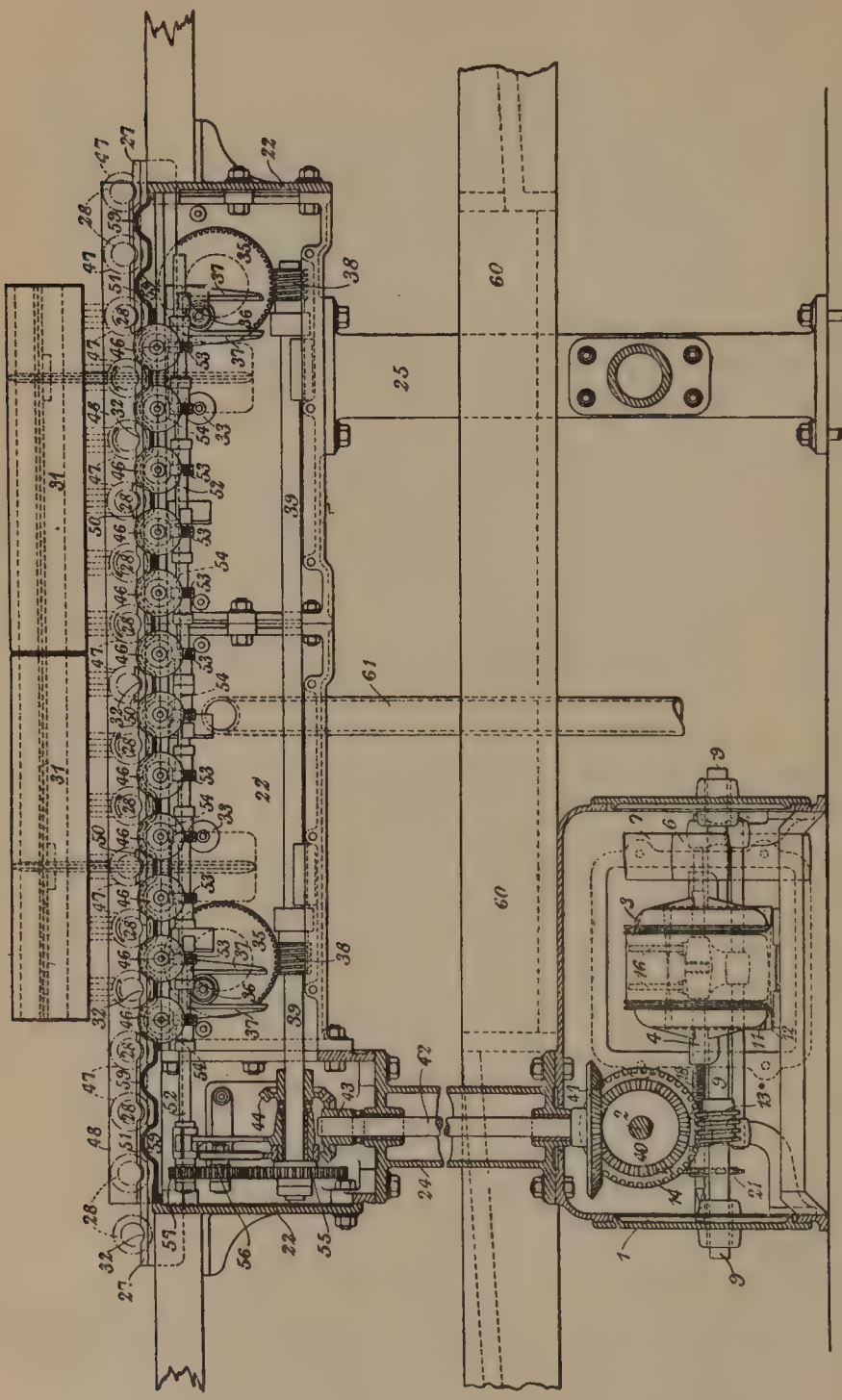


FIG. 24B.—Side Elevation of Skein-washing Machine.
(*English Patent* 9,067 *of* 1913.)

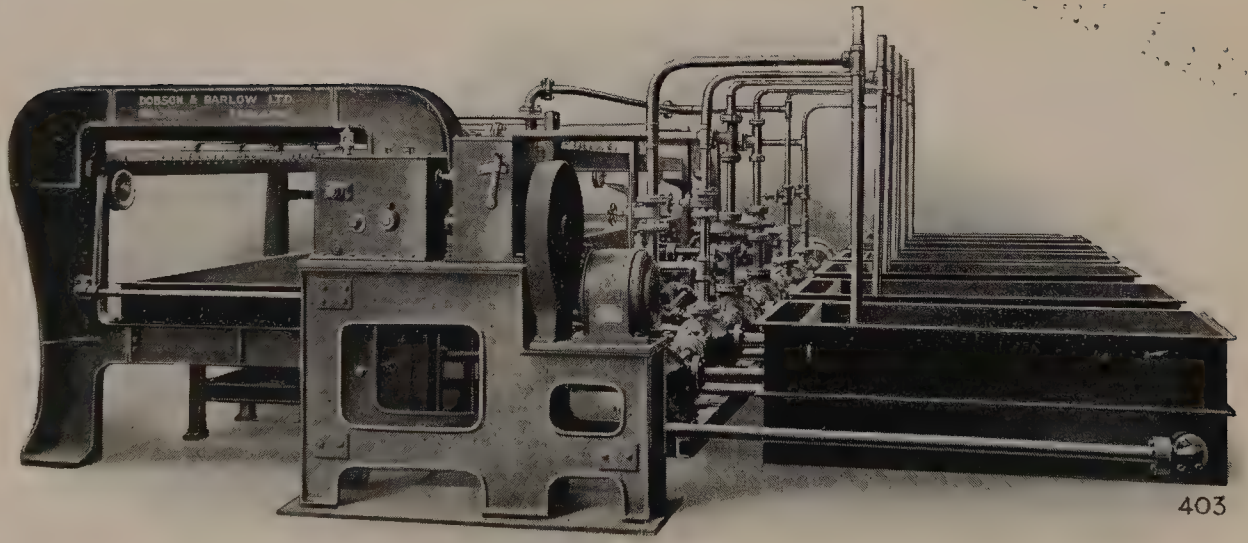


FIG. 25.—Skein-washing Machine

(*Dobson and Barlow, Ltd., Bolton.*)

[*To face p.* 47.

intermittently projected forward by the action of the rail *27*, which is alternately raised and lowered. The rate of travel is adjusted so that the skeins can be subjected to water or other liquids sprayed on to them from the tank *31*. The friction rollers *46* also impart rotary motion to the rods. They are generally arranged in groups of three, one group rotating in one direction and the next group in the opposite direction. By this means the threads of the skein are prevented from becoming entangled and are also evenly subjected to the action of the water or chemicals. A photograph of a typical up-to-date washing installation is shown in Fig. 25. The washing water is fed from the vats (shown at the sides) to the spray pipes. The quantity of water, as well as the rate of traverse of the skeins through the machine, is so arranged that complete washing of the skein is ensured. The water used for washing may be warm, and it should contain no calcium salts.

Stretching and Stoving.—The skeins coming off the washing machine are next placed in stretching frames, the skeins being suspended between smooth aluminium or duralumin rods, which are so arranged that tension can be applied to the skeins by varying the distance between the rods. A typical stretching machine is illustrated in Fig. 26, facing p. 48. The machine shown can take two rows of skeins; the toggles, actuated by screws by which the rods carrying the skeins are forced apart, are seen at the side of the machine. Drying is effected by allowing the stretcher frame to be propelled mechanically through a drying tunnel (Fig. 26, facing p. 48), which is fitted with disc fans, so that the air, heated by a number of gilled steam-pipes, circulates downwards through the skeins to avoid damage or entanglement of the skeins. The temperature maintained in the drying tunnel may range between 40° and 60° C. according to the particular factory (3). By the time the stretcher frame has arrived at the end of the tunnel the skeins

will be completely dried. An alternative installation consists of series of compartments capable of taking one or two stretcher frames. The frames remain in the compartment for a definite time, depending on the temperature and speed of air circulation (4). The stretching and stoving process effects the lustring of the silk. The object of the stretching is really to prevent contraction during the removal of the moisture. After drying, the skeins, as removed from the stretcher frame, are ready for subsequent treatment.

Bobbin-spun Threads.

In bobbin spinning the thread collected on the bobbins is untwisted, and therefore requires careful handling.

Washing.—Considerable difficulty was met with originally in effecting the complete removal of the adhering liquid from the spinning-bath. Washing the bobbins in running water removed only the acid and salts slowly. Recently it has been found that, if water is sucked through the thread from the outside, the washing is much more effective, can be carried out more rapidly, is more economical in water, and gives a thread which can be more easily reeled. Several devices have been patented for carrying out this so-called quick-washing process. Briefly, several perforated bobbins *2* are connected together by suitable devices *8*, closed at one end by a plug *4*, and placed in vats of water. By means of a plug *7* at the other end, carrying a pipe to which suction is applied, water is sucked from the outside through the thread (Fig. 27) (5).

Stoving.—The bobbins, after washing, are then stoved. The stoving is carried out under conditions similar to those already described for skeins (p. 47); the only difference is that the stretching of the thread is effected by the contraction and tightening of the thread on the bobbin. A frame of bobbins being placed in a stove is shown in Fig. 28, facing p. 49.

Humidifying and Twisting.—The dried bobbins,

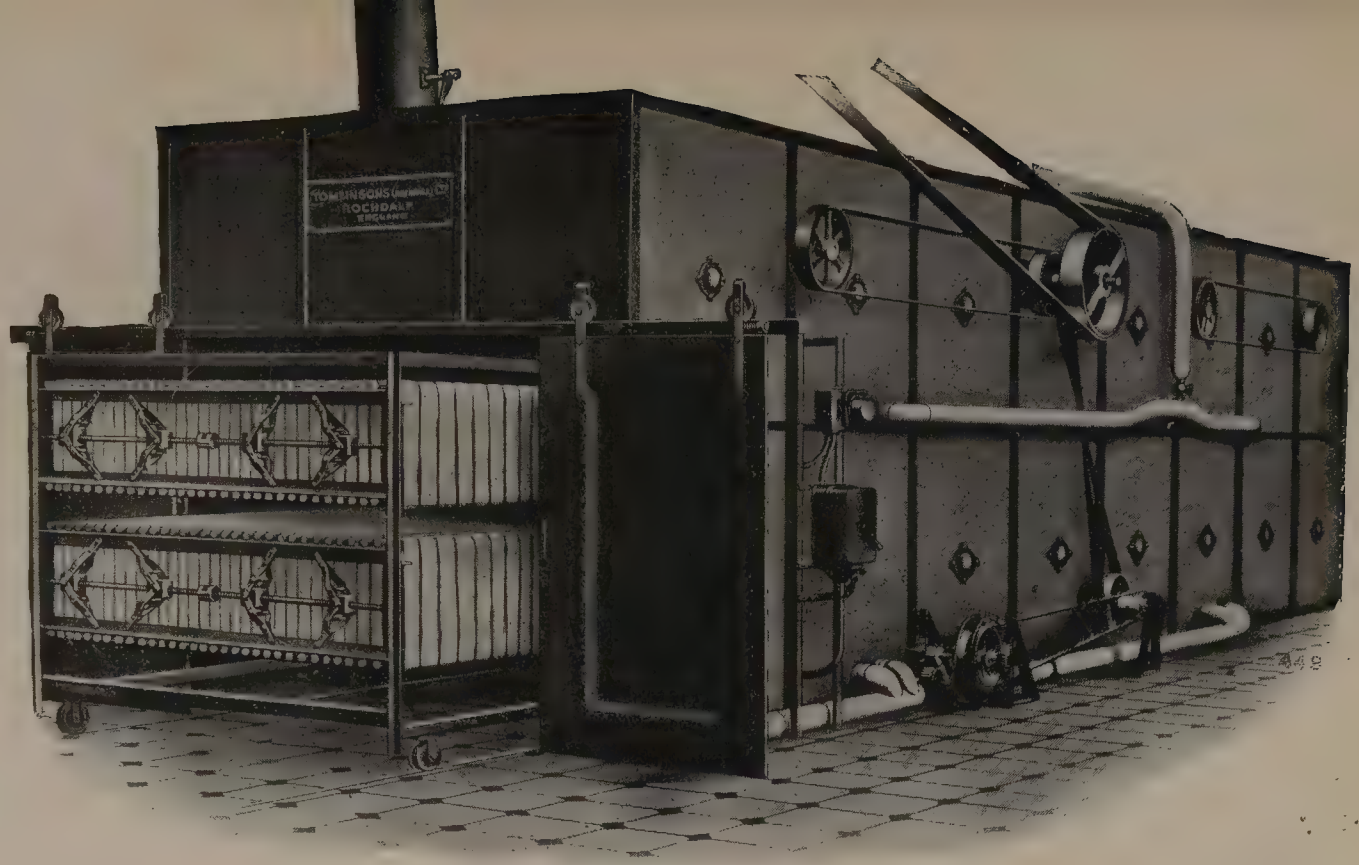


FIG. 26.—Skein Stretching Frame entering " Turblex " Tunnel Stoving Machine.
(*Tomlinsons (Rochdale), Ltd.*)

To face p. 48.

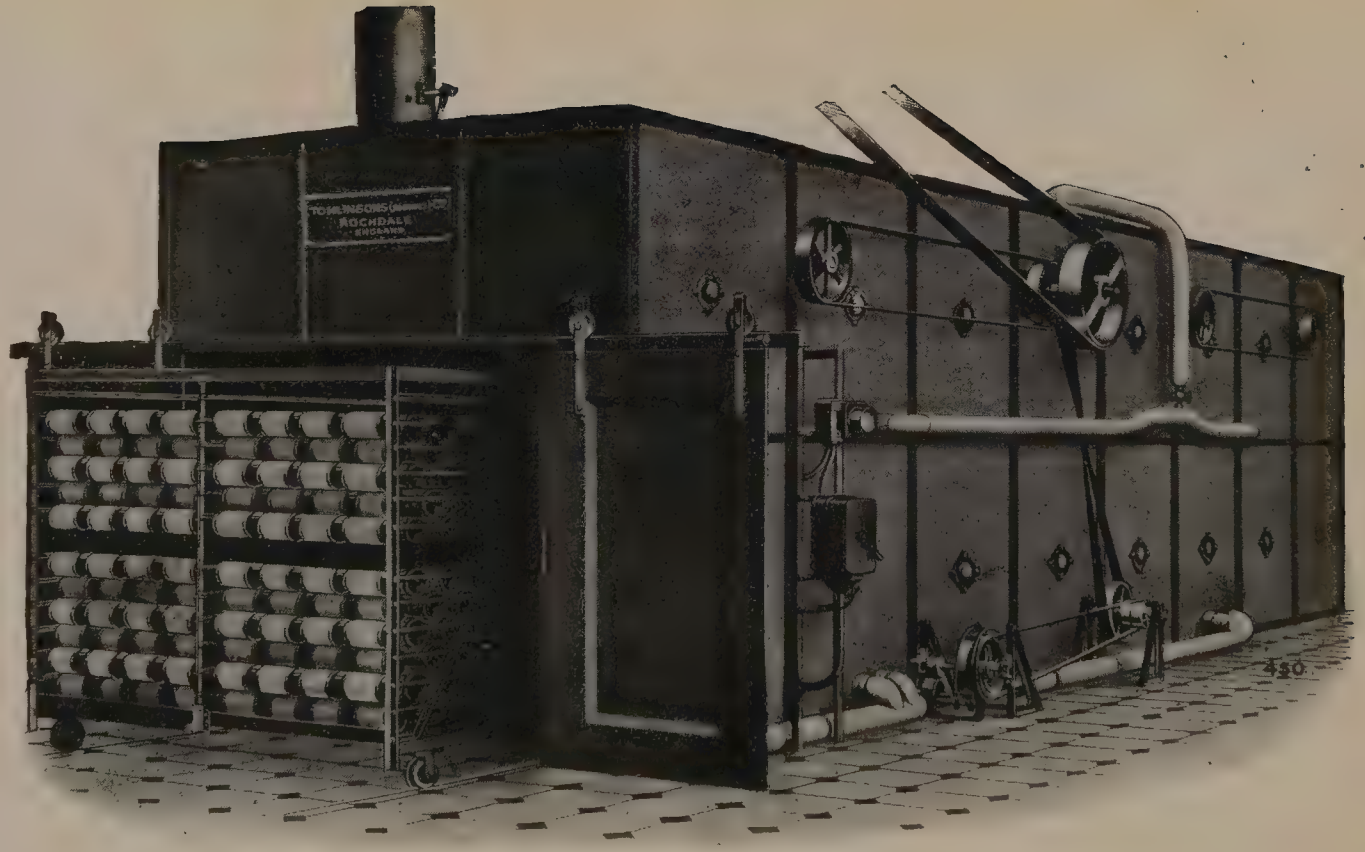


FIG. 28.—Frame of Bobbins entering "Turblex" Tunnel Stoving Machines.
(*Tomlinsons (Rochdale), Ltd.*)

[*To face p.* 49.

after leaving the stove, are placed in a suitable chamber to allow them to take up 8–10% of water before the twisting operation can be carried out. Twisting is carried out by placing the bobbins vertically on

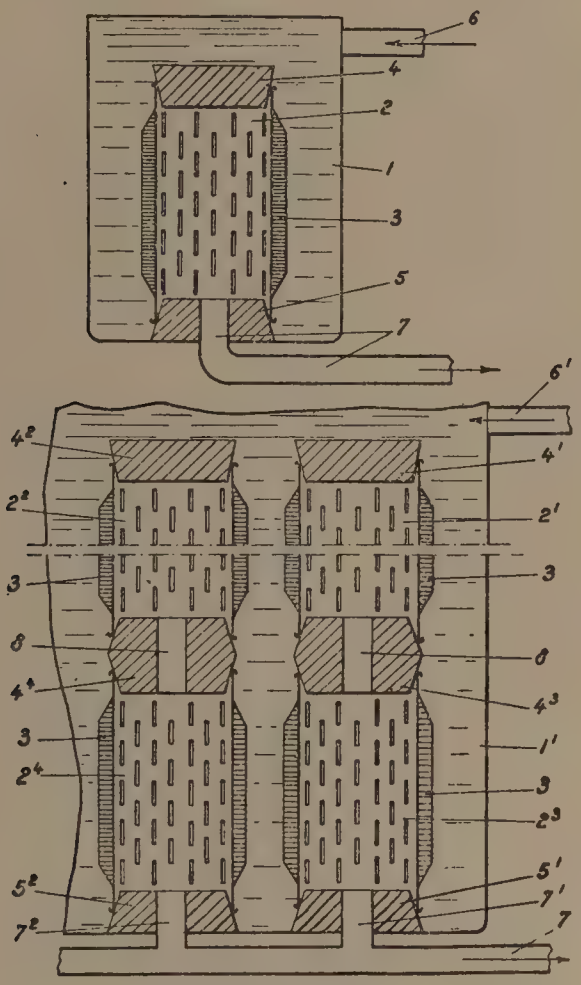


FIG. 27.—Method of Washing Bobbins.
(*English Patent* 239,482.)

spindles which can be rotated at a high speed. As the thread is unwound from the bobbin it is guided on to a bobbin rotating at a slower speed horizontally. The rapid speed of the lower bobbin causes the thread to "balloon," thereby imparting a twist; by adjusting the spindle speed of the lower bobbin and the peri-

pheral speed of the upper bobbin any required twist can be imparted. The relation of speeds and twist between the two bobbins is similar to that described for the box and godet speeds in the centrifugal spinning process (*cf.* p. 27). A section of a two-decker twisting machine capable of dealing with two rows of bobbins on each side is shown in Fig. 29.

Reeling and Lacing.—The twisted thread is, however, still wound on bobbins, and has now to be reeled into skeins. This is carried out by a similar machine to that described for reeling the "cakes" from the centrifugal spinning process, the bobbins standing in the place of the cakes.

After-treatment of Reeled Skeins.

From this stage the skeins produced by both processes are similarly treated, according as unbleached or bleached yarn is required.

Desulphurising.—The usual method of removing the sulphur from the thread consists in treatment with a solution of sodium sulphide (0·75–1%) at 40°–50° C. This dissolves out the sulphur, forming polysulphides; consequently the solution will gradually become rich in sulphur owing to the formation of sodium bisulphide and higher sulphides. Thus:

$$Na_2S + S = Na_2S_2$$
$$Na_2S_2 + S = Na_2S_3, \text{ etc.}$$

The higher sulphides do not so readily dissolve out the sulphur from the thread; consequently the solution gradually becomes less effective and must be changed. It has, however, been found that by adding an alkaline reducing agent the polysulphides can be reduced to the monosulphide.

In practice, proportionate quantities of sodium hydroxide and an organic compound (usually glucose) are continually added, according to the amount of thread treated in the bath, so that the quantity of polysulphide can be kept at a very low figure (6).

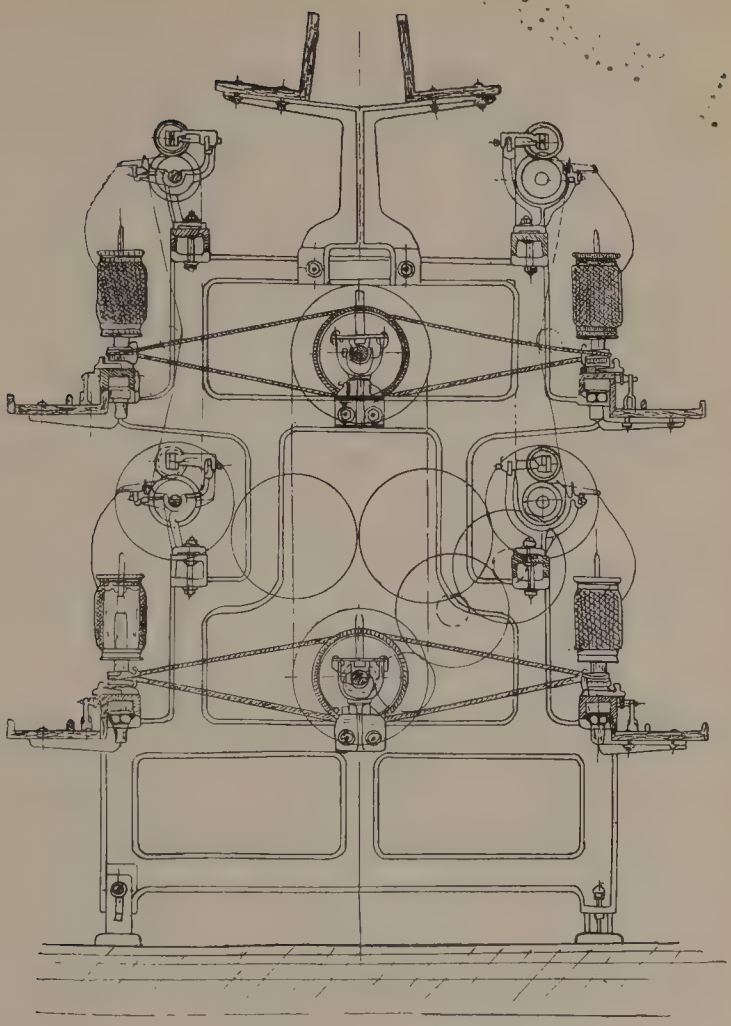


FIG. 29.—Two-decker Twisting Machine.

(*John Hetherington & Sons, Ltd., Manchester.*)

[*To face p.* 50.

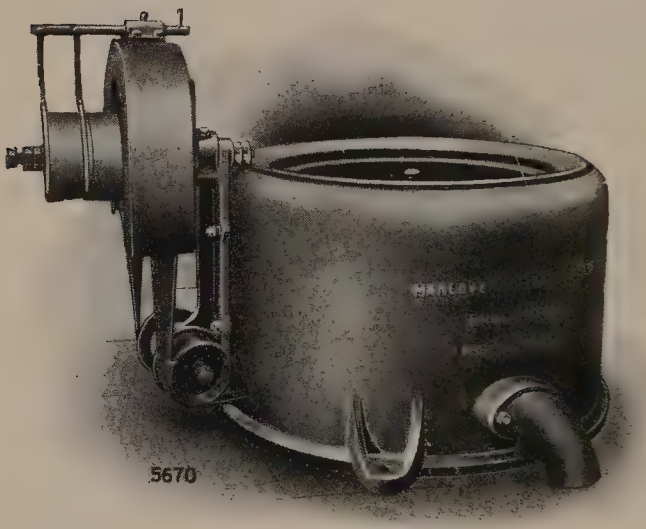


FIG. 30.—Hydro-extractor.

(*Manlove, Alliott & Co., Ltd., Nottingham.*)

[*To face p.* 51.

Washing. — After desulphurising, the skeins are washed thoroughly with water and then passed to the bleach bath.

Bleaching.—Bleaching is effected by the use of sodium hypochlorite solutions containing about 0·05–0·1% of available chlorine.

Souring and Washing.—The bleached skeins or, if bleaching is omitted, the washed skeins from the desulphurising process are next treated with dilute hydrochloric acid (0·5–0·6%), and then thoroughly washed.

The above operations, from desulphurising to final washing, are carried out in modern artificial-silk factories on one long machine (similar in construction to the washing machine, see p. 44), which is so arranged that the skeins, carried on ebonite-covered rollers, are saturated by overhead sprays with sodium sulphide, water, bleach and acid, arranged at definite sections of the machine. The rate of travel and the spraying of the liquids are so arranged that efficient desulphurising, washing, bleaching and souring are effected during the period the skeins traverse each particular zone of the machine.

Soaping or Sizing.—If soaped or sized yarn is required, the skeins are next soaped or sized in suitable baths. (For particulars of soap and size baths, see p. 94.)

Hydro-extracting.—The washed skeins are then wrapped up into bundles in suitable cloths and hydro-extracted in order to reduce the water content to the lowest possible amount. A typical machine for this purpose is illustrated in Fig. 30. The bundles of skeins are closely packed round the inside of the perforated basket of the hydro-extractor.

Drying and Humidifying.—The skeins are next hung loosely on pegs in a suitable drying-room, or they may be passed mechanically through drying chambers similar to those described for drying the skeins on the stretcher frames (p. 47). An installation can also be

provided with a humidifying zone at the end, so that the silk emerging at the end of the chamber will have the required moisture (about 10–12%).

It is generally preferable to dry the artificial silk at as low a temperature as possible (40°–50° C.) for a long period rather than at a higher temperature for a short period.

Movement of the threads of the skein by a current of air (velocity, 3–5 metres per second) during the drying is also stated to be beneficial, tending to give the artificial silk an increased bulk, and consequently greater covering power (7).

It has been proposed to dispense with initial stoving and stretching in the case of yarn spun by the centrifugal spinning process before desulphurising, etc., and to combine the stretching and stoving with the final drying when the artificial silk has been purified. This practice is being adopted abroad to a certain extent (8).

Sorting.—The finished artificial silk is now carefully examined, skein by skein, by trained operatives in a good light for colour, lustre, and absence of faults or blemishes, such as broken threads or filaments causing fluff, specks, and dull patches; it is then sorted into qualities accordingly. The weight of each skein is also checked, so that it may be sorted into correct sizes (deniers). Finally it is made up into 5, 10 or 20 lb. bundles, ready for despatch to the dyeing, weaving or knitting factories.

References.

(1) E. Wurtz. *Chemische Apparatur*, 1926, **13**, 262.
(2) Courtauld and Clayton. English Patent 9,067 of 1913.
(3) E. Wurtz. *Chemische Apparatur*, 1926, **13**, 282.
(4) *Engineering*, 1926, **122**, 659.
(5) Borzykowski. English Patent 239,482.
(6) Courtaulds and Wilson. English Patent 29,711 of 1912.
(7) W. P. Dreaper. English Patent 181,758.
A. G. Perl. *J. Textil. Inst.*, 1925, **16**, 195.
(8) W. P. Dreaper. English Patent 245,815.
Jentgen. *Die Kunstseide*, 1926, **8**, 295.

CHAPTER VI

CUPRAMMONIUM PROCESS

ALTHOUGH the proportion of the world's output of artificial silk produced by the cuprammonium process is to-day very small compared with that produced by the viscose process (see p. 4), yet for some purposes cuprammonium is superior to other artificial silks. The flow-sheet for the cuprammonium process is shown on the next page; a brief description of each stage will be given in so far as it is special to this process. The methods of spinning, reeling, bleaching and drying are generally very similar in all processes.

Preparation of the Solution.

Cellulose.—The cellulose used for cuprammonium solutions is generally cotton waste or linters, which has been suitably purified, as described in Chapters III (p. 17) and VII. Recently, however, specially purified sulphite wood-pulp has been successfully employed.

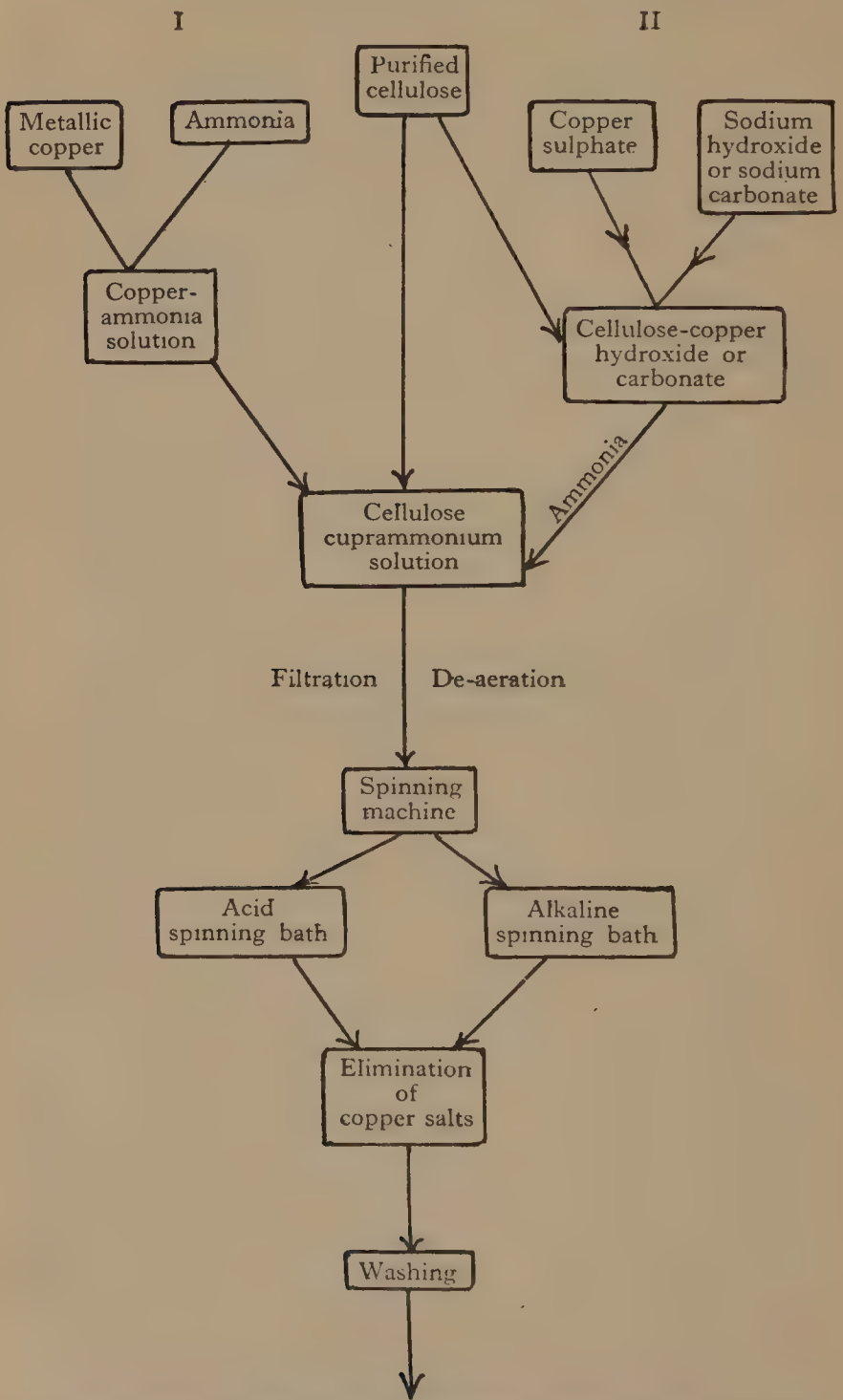
There are two general methods of making the solution, as indicated on the flow-sheet diagram, viz.:—

(*a*) From copper-ammonia solution.

(*b*) From copper-hydroxide or copper-carbonate ammonia solution.

(*a*) *Copper-Ammonia Solution.*—In the copper-ammonia method, which is the older and costlier process, metallic copper in the form of turnings or shavings is packed in a double-jacketed tower provided with means for blowing in air. The copper is saturated with strong aqueous ammonia and air is blown in. The air-ammonia mixture gradually attacks the copper and copper-ammonia solution is formed. Care is taken, by circulating chilled brine through the jacket of the tower, that

Flow-Sheet for Cuprammonium Process



Drying, twisting, reeling, bleaching, souring, washing, soaping sizing, hydro-extracting, drying, sorting.

the temperature does not exceed + 5° C. (1). The process is continued until the solution reaches the required strength in copper and ammonia, which may take fifteen to twenty hours. It is generally found advantageous to interrupt the blowing-in of the air at certain intervals during this period. The gravity of the finished solution should be about 1·004, and contain 3·0–3·5% copper and 25% ammonia.

The copper-ammonia solution thus obtained is now transferred to a suitable double-jacketed mixer and allowed to act at 4° C. on the purified cellulose so as to give a solution containing 8–10% cellulose. The type of mixer shown in Fig. 6 is quite suitable for this operation. In some cases a certain amount of sodium hydroxide is added to the copper-ammonia solution to assist the dissolution of the cellulose. There are many variations of this process, of which the object is to increase the solubility and economise the quantity of copper-ammonia required. It has been found that within certain limits an increase in the copper-content increases the solvent action of the solution on the cellulose, whereas a decrease in the ammonia-content ensures less degradation of the cellulose.

(*b*) *Copper - hydroxide Ammonia Solution.* — This method is largely used for the preparation of cuprammonium solution for spinning by the stretch-spinning process. It consists in the precipitation at 0° C. of copper hydroxide or carbonate by the action of sodium hydroxide or carbonate on a copper salt, *e.g.*, the sulphate. The voluminous precipitate thus formed is intimately mixed with the cellulose at 25°–30° C. in a suitable pulping machine, so that the penetration of the basic copper salt into the cotton is as complete as possible. The mixture is then filtered in a hydraulic press under considerable pressure to eliminate the sodium salts as much as possible. The cellulose copper-hydroxide cakes thus obtained are now treated in a mixer with a mixture of aqueous ammonia, sodium hydroxide, and in some cases organic compounds (*e.g.*,

glucose) to give a solution having the required cellulose-content and viscosity. The mixing takes several hours, and is carried out at a low temperature (0°–4° C.).

Filtration and De-aeration.—By whatever method the solution is obtained, it is next filtered several times through iron or nickel gauzes ranging from 120–200 mesh, and is then freed from air prior to being spun.

The solution is generally spun after twelve to seventy-two hours, but local practice varies considerably in this respect.

The cuprammonium solution is not stable, but gradually undergoes oxidation. By addition of caustic soda and organic hydroxy-compounds to the solution and keeping it at a low temperature, however, its instability is reduced to a minimum (2).

Method of Spinning the Solution.

Modern spinning of cuprammonium solution is in some respects similar to the spinning of viscose solutions ; thus the solution in a modern installation is fed through a pump to a jet containing a number of holes. The jets can be made of glass, nickel or steel (only when used in alkaline spinning baths). The thread is coagulated in an acid or alkaline bath and collected on glass or wooden bobbins (see p. 38). This bobbin method of spinning has been generally adopted for cuprammonium solutions, but in recent years an attempt has been made to use the centrifugal method of spinning (3).

Stretch-spinning Process.—In the description of viscose spinning reference has already been made to the stretch-spinning process, by which the thread is stretched or drawn out between the projection of the thread into the bath and the winding on to bobbins.

This process was originally put forward, and has been most successfully used for spinning of cuprammonium silk. Jets with comparatively coarse holes (0·25–0·75 mm. diameter, as against 0·05–0·1 mm. diameter) are used, and the threads projected from such

jets can be drawn out, so that filaments almost as fine as real silk can be produced (0·5–0·6 deniers per filament).

The apparatus, as described by Thiele in his original patent (4) (Fig. 31), consisted of a U-tube or vessel, each limb of which was jacketed. The solution emerged from the jet at *a*, and the thread was carried forward by its own weight down the left limb of the tube *b*, through a weak coagulating bath; it then passed up the right limb *d*, which contained the strong coagulating bath and emerged at the top and was drawn on to a bobbin.

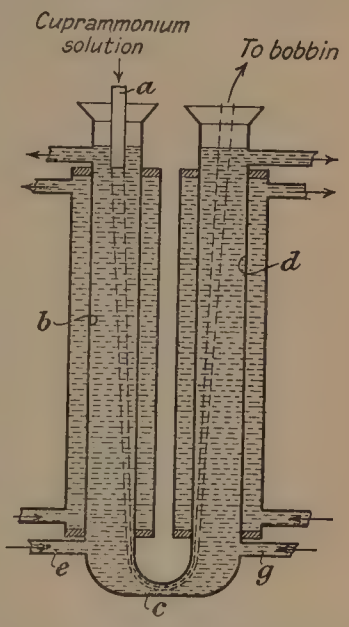


FIG. 31.—Thiele's Stretch Spinning Apparatus. (*English Patent* 8,083 *of* 1902.)

Modern practice has simplified this apparatus so that one vessel is now used, and the drawing out of the thread is effected by the slow countercurrent circulation of the weak coagulating bath; the thread is collected on a bobbin and coagulated by rotation in a stronger coagulating bath (5). In the diagram (Fig. 32) the coagulating liquid enters at *s*, and leaves at *d* and *r*, whilst the thread is formed at the jet *b*, and passes down the tube and emerges at *r*. By suitably arranging the flow at *s*, *d* and *r* a very gentle drawing out of the thread is effected. In a later patent (6) two or more jets are arranged in the same drawing-out funnel, suitable baffles being arranged to provide for the circulation of the spinning bath (see Fig. 33).

This drawing out of the threads is generally effected by using two baths, the first being the weaker one. Ingenious methods have been devised for carrying out this method, so that the thread from the jet progresses

through a column of liquid gradually increasing in strength. The thread emerging from the bath is either collected on suitable bobbins or in a centrifugal receiver, in which it is twisted as in the viscose process.

Spinning-bath.—(*a*) *Acid Baths.* Acid baths containing 10–50% H_2SO_4 at ordinary temperatures were formerly used for spinning cuprammonium silk. Such baths are, however, not so generally used to-day for

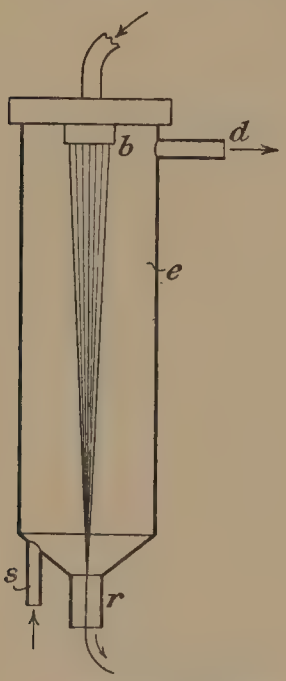


FIG. 32.—Bemberg's Stretch-spinning Apparatus. (*English Patent* 224,864.)

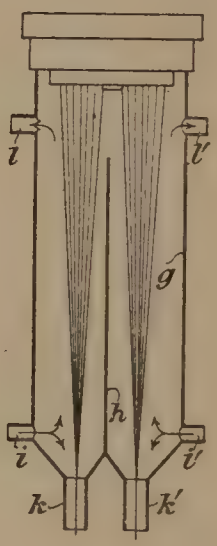


FIG. 33.—Bemberg's Stretch-spinning Apparatus. (*English Patent* 246,335.)

the initial coagulation with the stretch-spinning methods.

(*b*) *Alkaline baths.* The alkaline spinning baths may consist of sodium hydroxide solutions (5–30% NaOH) and an organic compound, such as glucose (7–8%); such baths may be allowed to act between 0°–50° C., according to the particular composition used. In the stretch-spinning process a dilute alkali bath (5% NaOH) is followed by a stronger alkali or an

acid bath. In a recent patent a spinning bath of water at 20° C. followed by a bath containing alkalis and salts at 50° C. has been advocated (7).

After-treatment of Spun Thread.

Elimination of Copper.—The alkali-coagulated thread is blue in colour, owing to the presence of a copper compound, and has therefore to be subsequently treated with acid (5–10% sulphuric acid).

From the acid-spun thread in bobbin-spinning most of the copper compounds are removed while the bobbin collecting the thread is rotating in the second bath.

Finishing.—The thread produced by either process is washed free from acid and dried on the bobbin, or in the form of skeins, in exactly the same manner as described for the thread produced from viscose.

After stretching, the thread (if on bobbins it is next twisted and reeled into skeins) is bleached, soaped, dried and sorted, as already described.

The economical working of the cuprammonium process depends largely on the successful recovery of the copper compounds and, to a less extent, of the ammonia.

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(1) VERMEESCH. English Patent 20,408/1906.
BRONNERT, FREMERY and URBAN. English Patent 1,763/1900.
(2) BRONNERT. *J. Soc. Dyers and Colourists*, 1922, **38**, 153.
Textile Mercury, 1927, **77**, 210.
(3) BEMBERG. English Patent 260,564.
(4) THIELE. English Patent 8,083/1902.
(5) BEMBERG. English Patents 224,503 and 224,864.
(6) BEMBERG. English Patent 246,335.
(7) BEMBERG. English Patent 244,492.
See also books referred to at the end of Chapter III.

CHAPTER VII

NITROCELLULOSE PROCESS

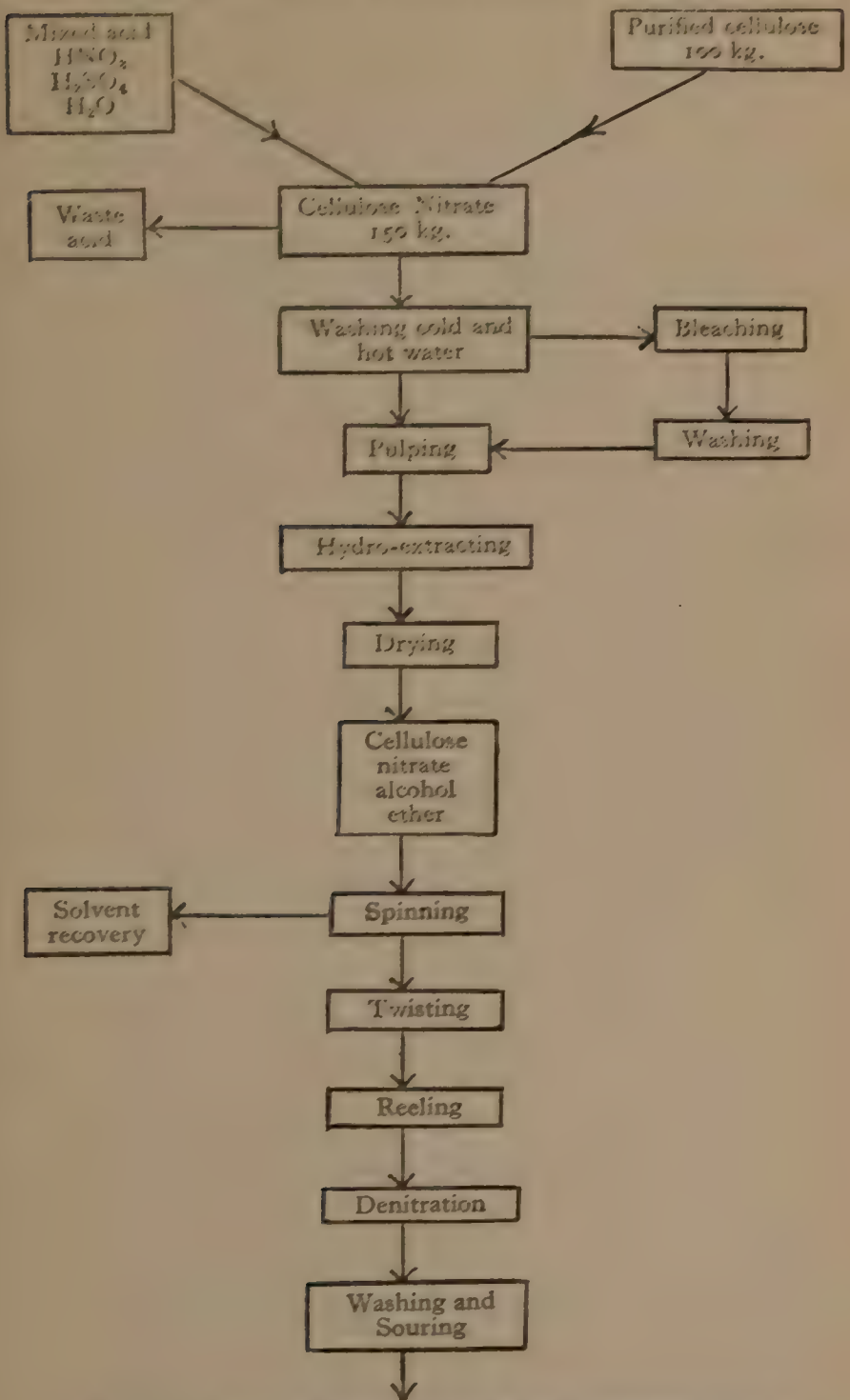
THE nitrocellulose process is unique in that it has been closely studied in all countries, because nitrocellulose is the basis of very many explosives. Consequently it is not surprising to find that the effects of varying such factors as temperature and duration of nitration, the composition of the nitrating mixture and the proportions of cellulose to acid are well known in regard to their effect on the nitrogen-content and solubility of the nitrocellulose produced. Moreover, plant for carrying out the nitration process is more or less standardised throughout the world. Nevertheless, the world's production of artificial silk by the nitrocellulose process to-day is on the wane and is likely to diminish still further. The flow-sheet for the process is shown on the opposite page, and is followed by a brief description of the several stages which are special to it.

Preparation of Cellulose Nitrate.

(*a*) *Cellulose*.—The raw material used for nitration is generally purified cotton waste or cotton linters. Wood-pulp in the form of special crêpe paper can also be nitrated successfully, but it has not been used to any extent in artificial-silk manufacture.

The purification of cotton cellulose is of considerable importance in connection with the manufacture of explosives, and is carried out under carefully-controlled conditions. First, the cotton has to be freed from oil, etc., and this is usually effected by extraction with organic solvents such as benzol or the chlorinated hydrocarbons (*e.g.* chloroethylenes). The extracted material, freed from solvent, is then boiled in stationary

Flow-Sheet for Nitrocellulose Process



Bleaching, souring, washing, soaping, sizing, hydro-extracting, drying, sorting.

or revolving kiers with a weak solution of sodium hydroxide (3%), or a solution containing sodium hydroxide (3%) and sodium carbonate (3%) for four to ten hours under a pressure of 15–20 lb. per square inch. In some cases boiling is carried out in open kiers with similar strengths of alkali. This boiling effects the removal of cotton wax and any non-cellulose impurities, especially in the case of linters. After boiling the cotton is washed free from alkali, bleached, soured, washed and dried. The dried cotton is then usually opened out by passing through a "teasing" machine, which consists of a rapidly rotating drum provided with iron teeth. Variations in the conditions of kiering have been found to modify the viscosity of the resulting nitrocellulose when dissolved in ether-alcohol. Consequently the conditions of the purification process are kept as constant as possible in order to obtain solutions of similar viscosity for spinning. A typical analysis of cotton thus purified is given on p. 18.

(*b*) *Mixed Acid.*—The purified dried cotton is nitrated by means of a mixture of nitric and sulphuric acids. The composition of the mixed acid, the temperature, time of nitration, and the proportion of acid to cellulose can be varied between fairly wide limits to obtain the cellulose nitrate with a maximum solubility in ether-alcohol (nitrogen content, 11·3–12·5%; see p. 10).

In the following table are given three typical examples of the conditions in use for the nitration of cellulose for artificial-silk production (1):—

Time of nitration	Temp. of nitration	% Composition of Mixed Acid		
		HNO_3	H_2SO_4	H_2O
1 to 1·5 hr. . .	40° C.	37·5	48·0	15·0
10 min. . . .	50° C.	31·5	53·8	14·7
20 to 30 min. . .	30° C.	17·0	66·0	17·0

The proportion of mixed acid to cellulose may vary between 25–60 : 1.

(*c*) *Apparatus Used.* — There are three general methods employed in practice for the carrying out of the nitration process. These may be classified as the—

(i) Pot process.
(ii) Centrifugal process.
(iii) Displacement process.

(i) *Pot Process.*—In this method the cotton is carefully added to the nitrating acid, contained in cast-iron vessels holding about 200 lb. of acid, which can be kept cool, and the nitration allowed to proceed at a definite temperature for the specified time. At the end of the nitration the contents of several pots are poured into centrifugals. By this means as much acid as possible is recovered, and then the nitrated cotton is washed in the centrifugal or " drowned " in a large quantity of cold water.

(ii) *Centrifugal Process.*—In this process the whole operation of nitration is carried out in a centrifugal, the basket of which is lined with acid-resisting material. At the end of the nitration period the mixed acid is run off, and the basket is then revolved to eliminate as much of the remaining acid as possible. Washing can be effected by spraying in water during the rotation of the basket. By this process less handling is involved and a greater quantity of cotton can be nitrated in a batch.

(iii) *Thomson Displacement Process.*—Nitration is carried out in large, shallow earthenware pans, and at the end of nitration the acids are slowly displaced by a stream of cold water flowing in at the top of the nitrating pan.

This method, though possessing considerable advantages, has not, however, been widely adopted in foreign countries.

Washing.—The preliminary washing or drowning of the nitrated cellulose in cold water has already been referred to. Washing has also to be continued till the material is quite free from acid. Final washings are carried out with hot water.

Pulping.—The material is next transferred to a pulping machine, in which, by means of a rotating bronze cutter, it is reduced or pulped in water to small fibres about 1 mm. in length; this operation may take several hours. The cellulose nitrate may be bleached during pulping or washing, if required.

Hydro-extracting and Drying.—The pulped cellulose nitrate is finally hydro-extracted and dried (to a moisture content of 12–20%) in vacuum or other drying chamber at 40°–50° C.

Preparation of the Spinning Solution.

The usual solvents for the cellulose nitrate are mixtures of alcohol and ether, and their proportions depend on the required strength of the cellulose nitrate solution and the method by which the solution is to be spun, *i.e.*, by the wet or dry method of spinning. In the wet spinning (see below) a weak solution of cellulose nitrate (*i.e.*, 10%) is used, and consequently the proportion of ether is kept to a minimum (*e.g.*, 94% methyl alcohol, 2% ethyl alcohol, 4% ether). In dry spinning a solution containing 18–25% cellulose nitrate may be used, the solvent being a mixture of ether (60–40) and alcohol (40–60).

Between these limits the ratio of alcohol to ether may vary considerably. The proportion of water in the cellulose nitrate may also be varied, and considerable differences are met with in this respect in practice. The dissolution of the cellulose nitrate in the mixture of ether-alcohol is carried out in suitable mixers, and may take several hours. The solution thus obtained is filtered several times through cotton wool, silk and metal gauzes and de-aerated.

Methods of Spinning the Solution.

There are two methods of spinning nitrocellulose solutions for the production of artificial silk :—

(*a*) Wet-spinning.
(*b*) Dry-spinning.

(*a*) *Wet-spinning*.—The wet-spinning method is similar to that described for viscose and cuprammonium spinning, *i.e.*, the thread is coagulated in suitable setting baths and collected on bobbins or in centrifugal spinning-boxes. In the case of nitrocellulose, bobbin spinning is generally employed, the coagulating bath usually being water. This method of spinning enables the solvents to be recovered fairly economically and simply. It is, however, rather slow, but has the advantage that lower pressures for the forcing of the thread through the jets are required. This method of spinning has, however, not been so extensively used as the dry-spinning method.

(*b*) *Dry-spinning*.—In the dry-spinning method no coagulating bath is used, but the solvent is evaporated spontaneously by warm air, so that as the solution is forced through the jets it solidifies forthwith, and is collected directly on a bobbin or in a centrifugal spinning box (2). It is necessary to use a readily volatile solvent (generally one containing a large proportion of ether), and also comparatively small holes in the jet (0·5–0·1 mm. diameter). In comparison with the wet-spinning method, owing to the high percentage of cellulose nitrate in the solution, the output per jet in a given time is considerably greater, and the amount of solvent required is correspondingly less. On the other hand, the recovery of the solvent, on which the economic success of the whole process depends, requires more complicated plant.

After-treatment of the Spun Thread.

The subsequent treatment of the nitrocellulose thread is similar by whatever method spinning is carried out.

It consists in the operations of twisting, reeling, denitration and purification of the thread.

Denitration.—The reeled skeins are now subjected to a denitrating bath to convert them into cellulose. Various methods have been suggested for denitrating, but the most satisfactory reagents have been found to be the hydrosulphides of calcium, sodium, ammonium, or magnesium (3). The first two salts are generally used in practice. Denitration has to be carried out under very carefully-controlled conditions as to temperature and duration of the process, so as to ensure complete evenness and uniformity of the finished product in respect of such properties as dyeing, feel and lustre. A bath containing 5% sodium hydrosulphide may effect denitration at 40° C. in one to two hours. The denitration process is controlled by the titration of the contents of the bath and examination of the thread.

Various additions to the denitrating bath have been suggested, but such additions are not generally recommended. The denitrated thread still contains about 0·05% nitrogen, and has also suffered a reduction in weight. Consequently, to obtain a given denier of artificial silk, it is necessary to spin a thread correspondingly greater in size to allow for this reduction (*e.g.*, 150 denier cellulose-nitrate thread corresponds to about 100-denier finished artificial silk).

Finishing.—After denitrating, the thread is washed and soured with hot dilute hydrochloric acid to remove any iron sulphide, then bleached, soured, washed, soaped and dried as described for the other processes.

Mixed Acid and Solvent Recovery.

As has already been stated, the successful working of the nitrocellulose process depends very largely on the efficient recovery of the chemicals used in the process, viz. :—

(*a*) The mixed acids.
(*b*) The solvents used for dissolving the nitrocellulose.

It is not proposed to consider the problem of acid-recovery, as it is very fully discussed in treatises on explosives manufacture.

The recovery of the solvent ether-alcohol has also been worked out very carefully, a compression or a solvent method being employed. At the most, however, not more than 70–80% can be successfully recovered. The extended use of activated charcoal for this purpose offers promise of a slightly better recovery (2).

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MARSHALL. "Explosives," 1917, Vol. I., pp. 168–181.
(2) JENTGEN. *Die Kunstseide*, 1926, **8**, 295.
(3) DULITZ. *Chem. Ztg.*, 1910, **34**, 989.

CHAPTER VIII

CELLULOSE-ACETATE PROCESS

ARTIFICIAL-SILK manufacture from cellulose-acetate solutions differs from the processes hitherto described in that the finished thread is still a compound of cellulose, and as such has properties different from those of other artificial silks (see Chapter X).

The manufacture of cellulose acetate has been carried on for a number of years on the Continent, and during and since the war in this country, but its utilisation for the production of artificial silk on a large scale is a very recent development. It is even now too early to say whether its manufacture will survive the test of time, though it is interesting to note that one of the largest manufacturers of artificial silk by the viscose process in this country is also commencing the manufacture of cellulose-acetate artificial silk.

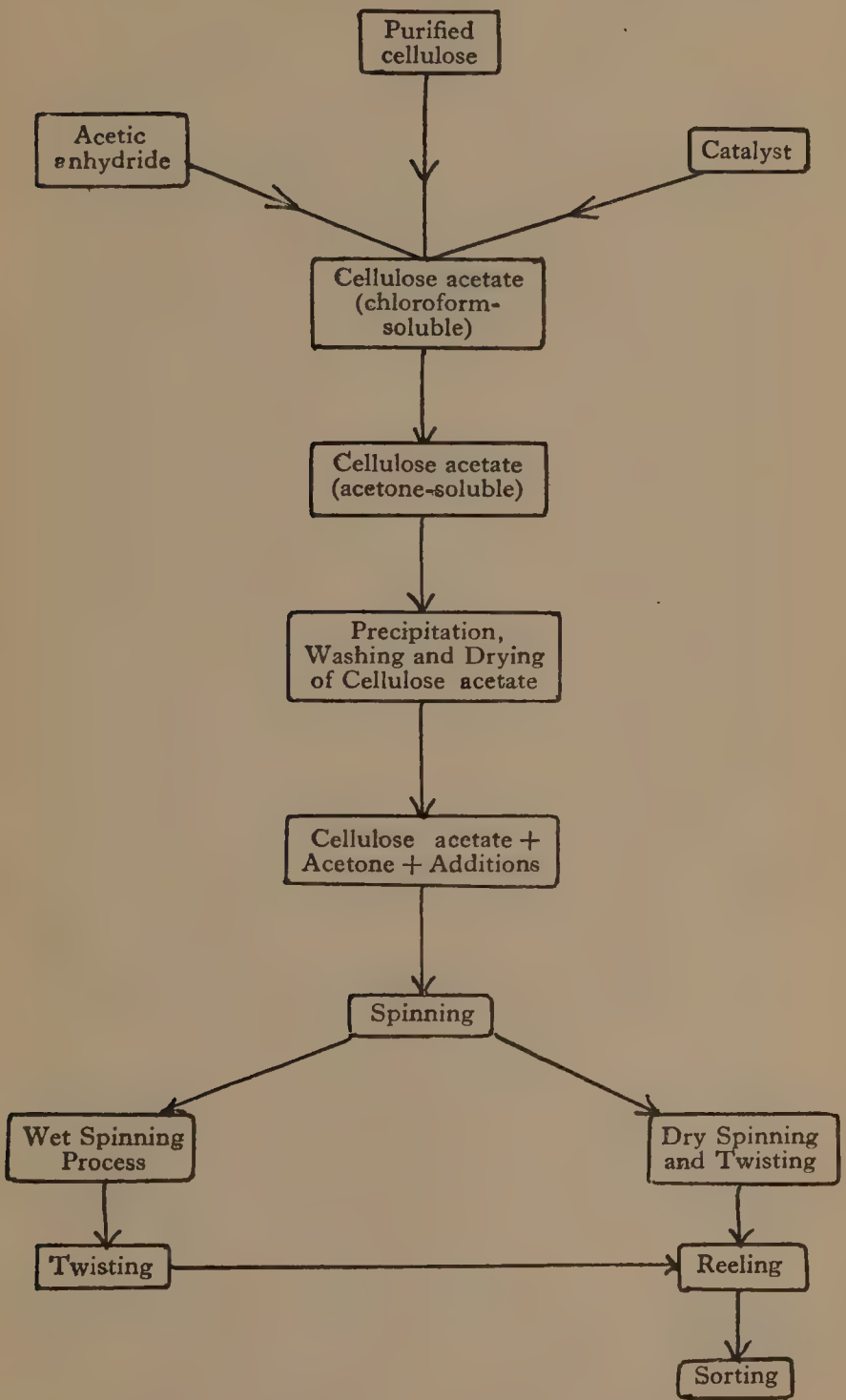
It will be noticed from the flow-sheet on the opposite page that the cellulose-acetate process is comparatively simple.

Preparation of Cellulose Acetate Solution.

Cellulose.—Cotton waste or linters are generally employed, but wood-pulp can be used ; the methods of purification are similar to those already referred to in the description of the nitrocellulose process (p. 60).

Acetylation.—The cellulose, which should not contain more than 5–6% water, is heated in a suitable jacketed mixer, provided with a stirrer, with a mixture of acetic acid and acetic anhydride in the presence of a catalyst, such as sulphuric acid or zinc chloride. The duration of the acetylation process depends on the temperature of the reaction, the composition of acetylating mixture, and the catalyst used ; and these

Flow-Sheet for Cellulose-Acetate Process



factors can be varied within fairly wide limits. A large number of catalysts other than the two mentioned have been proposed.

The acetylating mixture usually contains equal weights of acetic anhydride and acetic acid and about 5–20% sulphuric acid, or 60–70% zinc chloride on the weight of cellulose. Acetylation may be carried out between 25°–70° C., and the duration of the action may be between three and forty-eight hours (1).

Hydration.—At the end of the reaction the cellulose acetate that is dissolved in the reaction mixture should be soluble in chloroform, but insoluble in acetone. In order to convert the compound into the acetone-soluble compound, which is required for artificial silk or film manufacture, the acetylating mixture is usually mixed with a further quantity of acetic acid (water and sulphuric acid may also be added), and the reaction mixture is heated up to and maintained at 50°–70° C. for some hours (2).

Precipitation and Dissolution.—The cellulose acetate is now precipitated from the reaction mixture by dilution with water ; it is well washed and hydro-extracted, dried, and dissolved in a suitable solvent for spinning, filtered and de-aerated.

Method of Spinning the Solution.

Two methods of spinning can be used :—

(*a*) Wet-spinning.
(*b*) Dry-spinning.

In the former method a solution of the cellulose acetate in acetone or other solvent can be spun into baths of hydrocarbons, oils, or aqueous solutions of salts (3). By the use of suitable coagulating baths the stretch-spinning process can be used (4). It has been suggested that the acetylating mixture itself can be suitably diluted and spun direct. In wet-spinning the thread is collected on bobbins, washed, twisted and reeled, as previously described for other processes.

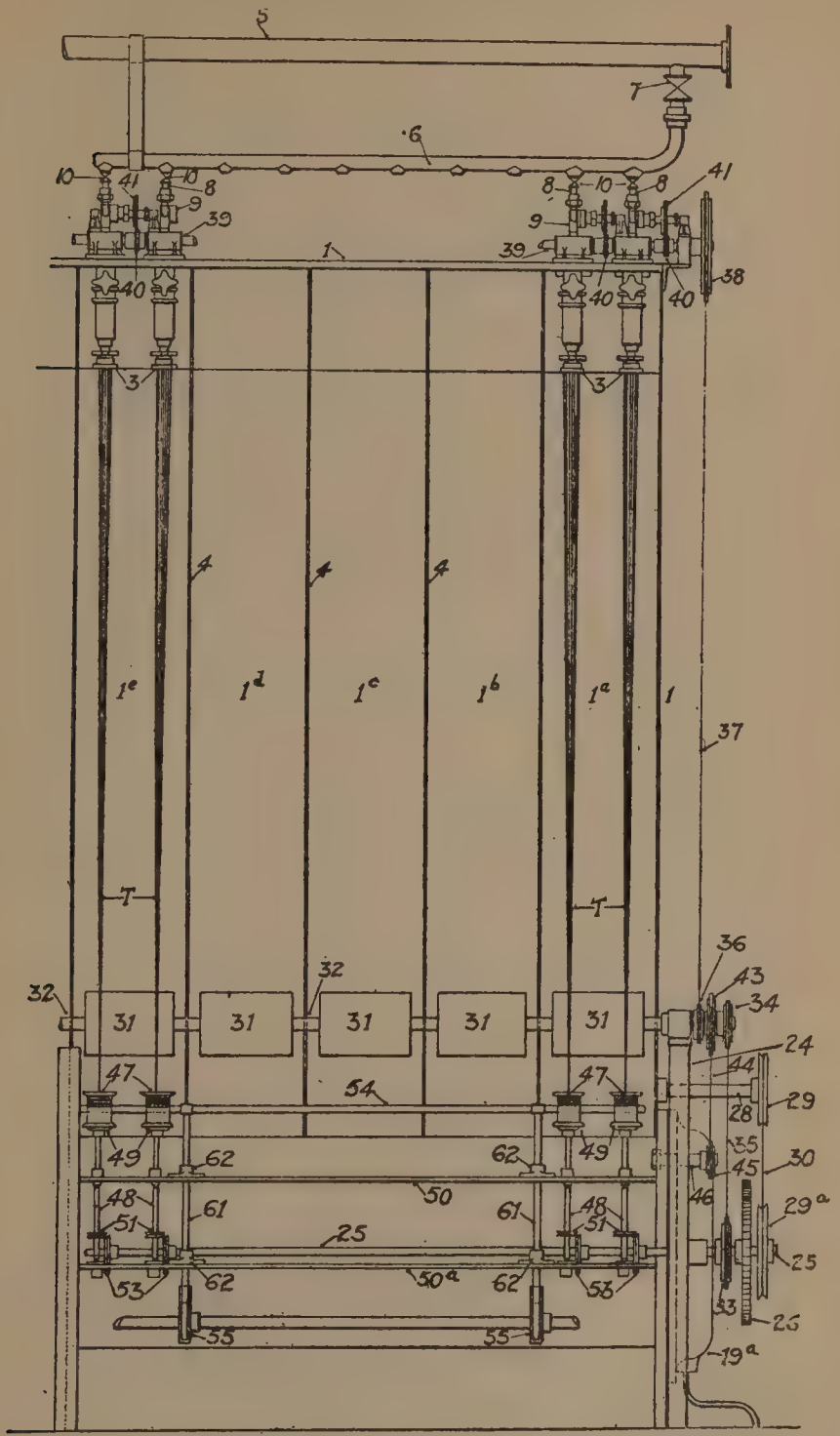


FIG. 34A.—Sectional Elevation of Dry-spinning Bobbin Machine.
(*English Patent* 165,519.)

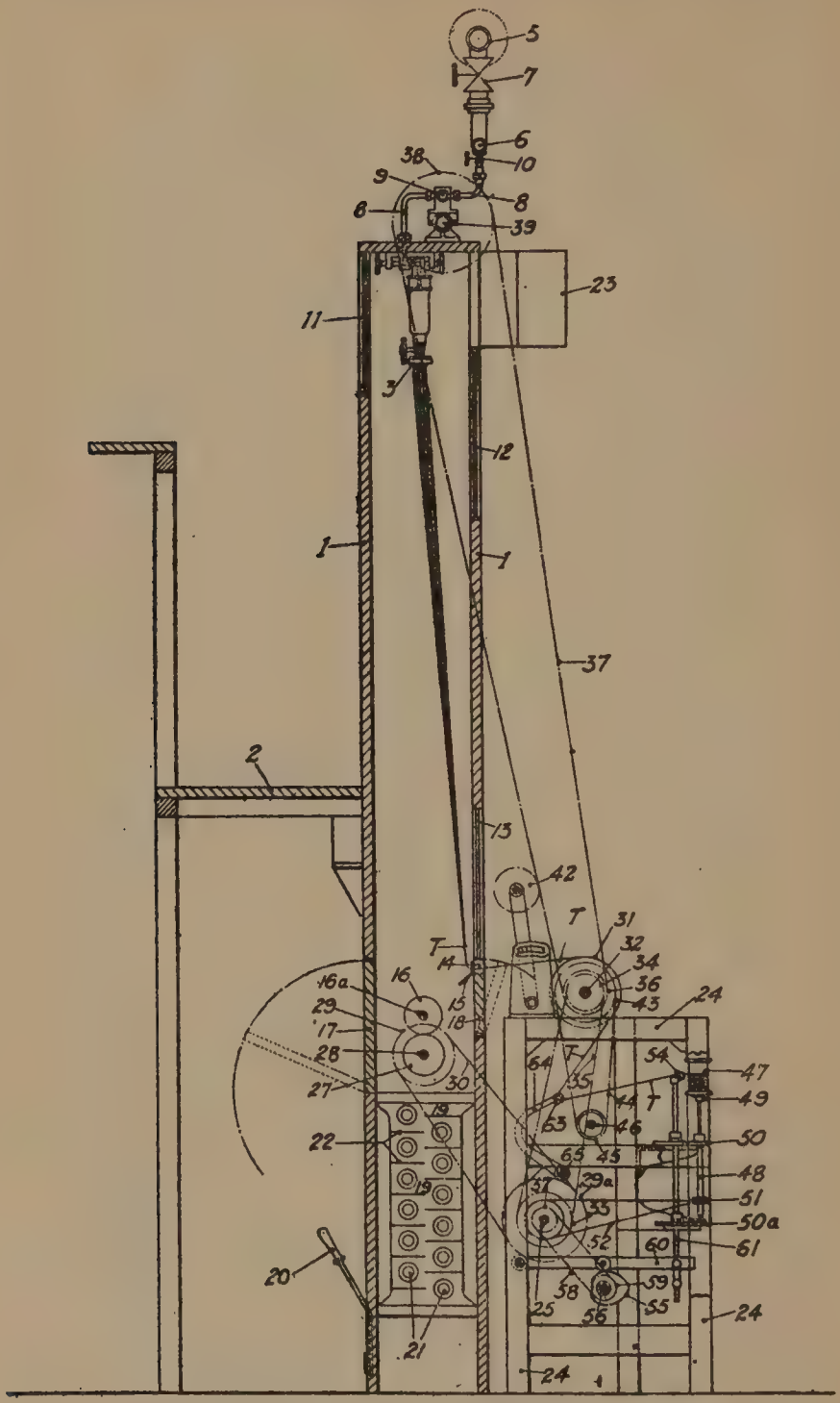


FIG. 34B.—Side Elevation of Dry-spinning Bobbin Machine.
(*English Patent* 165,519.)

In the dry-spinning method the acetone or acetone-alcohol solution containing 5–20% cellulose acetate is projected into a closed compartment, and the solvent is evaporated by hot air. Suitable mixtures of acetone and aldehyde, acetone and alcohol, acetone and other compounds have been suggested to enable the rate of evaporation of the solvent, and hence the solidification of the thread, to be controlled. By this means the partially solidified thread at the jet can be drawn out and very fine filaments produced, as in the stretch-spinning process (*cf.* p. 57) (5).

In Figs. 34 A and B, is shown an ordinary dry-spinning installation for collecting the untwisted thread on bobbins. The solution passes through the pump *9* and a filter to the spinning jets *3* into vertical compartments *1* heated by steam pipes *21*. The thread passes out at the opening *14*, and is collected on the bobbin *31*. The thread thus obtained usually requires little or no after-treatment except twisting and reeling into skeins.

Recently it has been found possible to make the spinning and twisting processes one continuous operation, so that the finished thread is collected on to bobbins or pirns (cap spinning) (6).

Figs. 35 A and 35 B represent an installation for this purpose ; the thread passes out at the opening *5*, over and under the godet roller *7*, and is then guided under the cap *20* and on to the bobbin, which rotates at a high speed and also has a slow vertical motion. By this means the thread receives the twist required, depending on the spindle speed of the bobbin and the rate of feeding on the thread. If the cellulose-acetate silk is required in the form of skeins it is reeled from the bobbins in a separate operation.

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(1) Levy. English Patents 213,631 ; 240,624.
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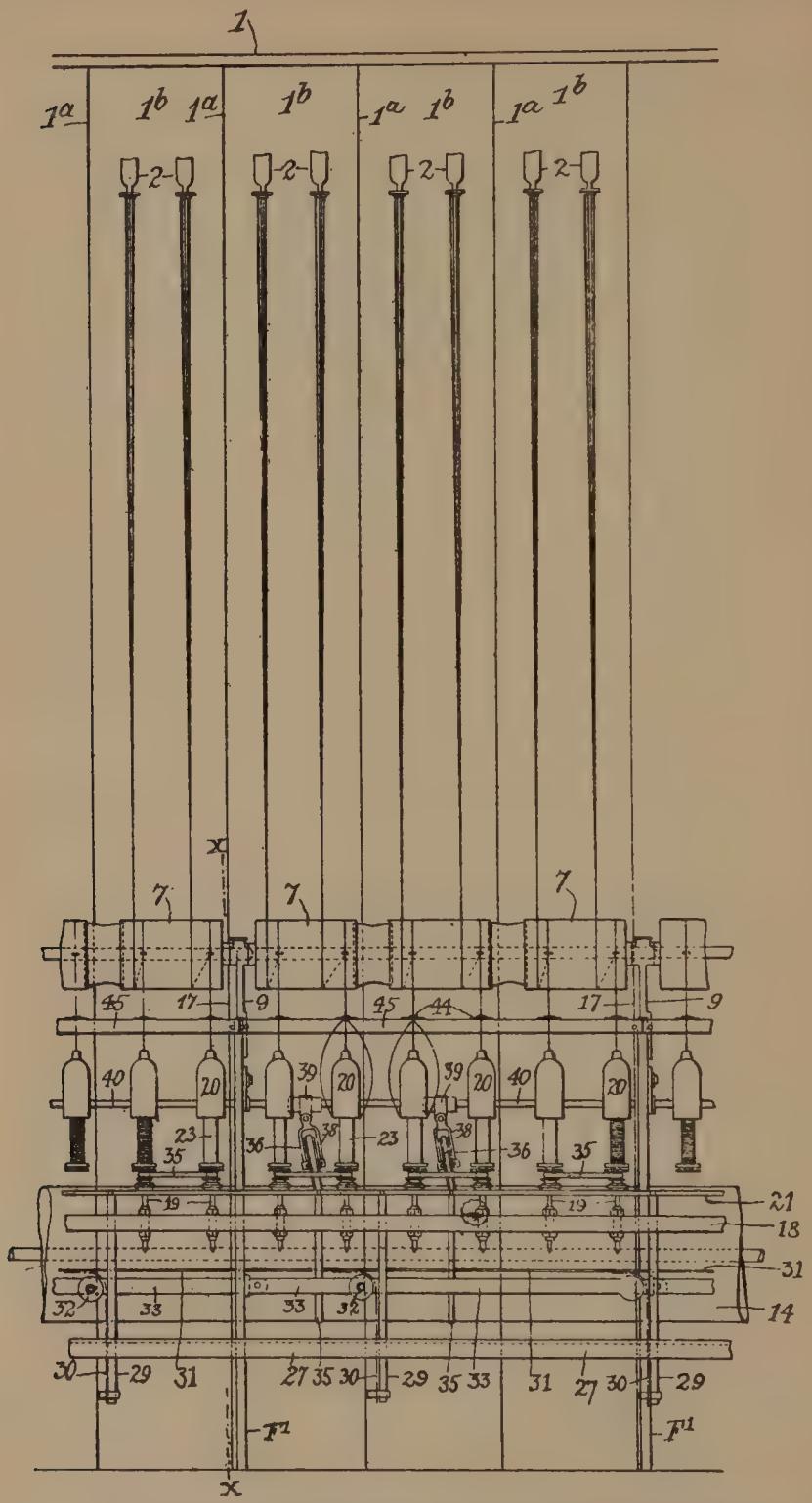

FIG. 35A.—Sectional Elevation of Dry-spinning Machine with Cap-spinning Collecting Device.

(*English Patent* 198,023.)

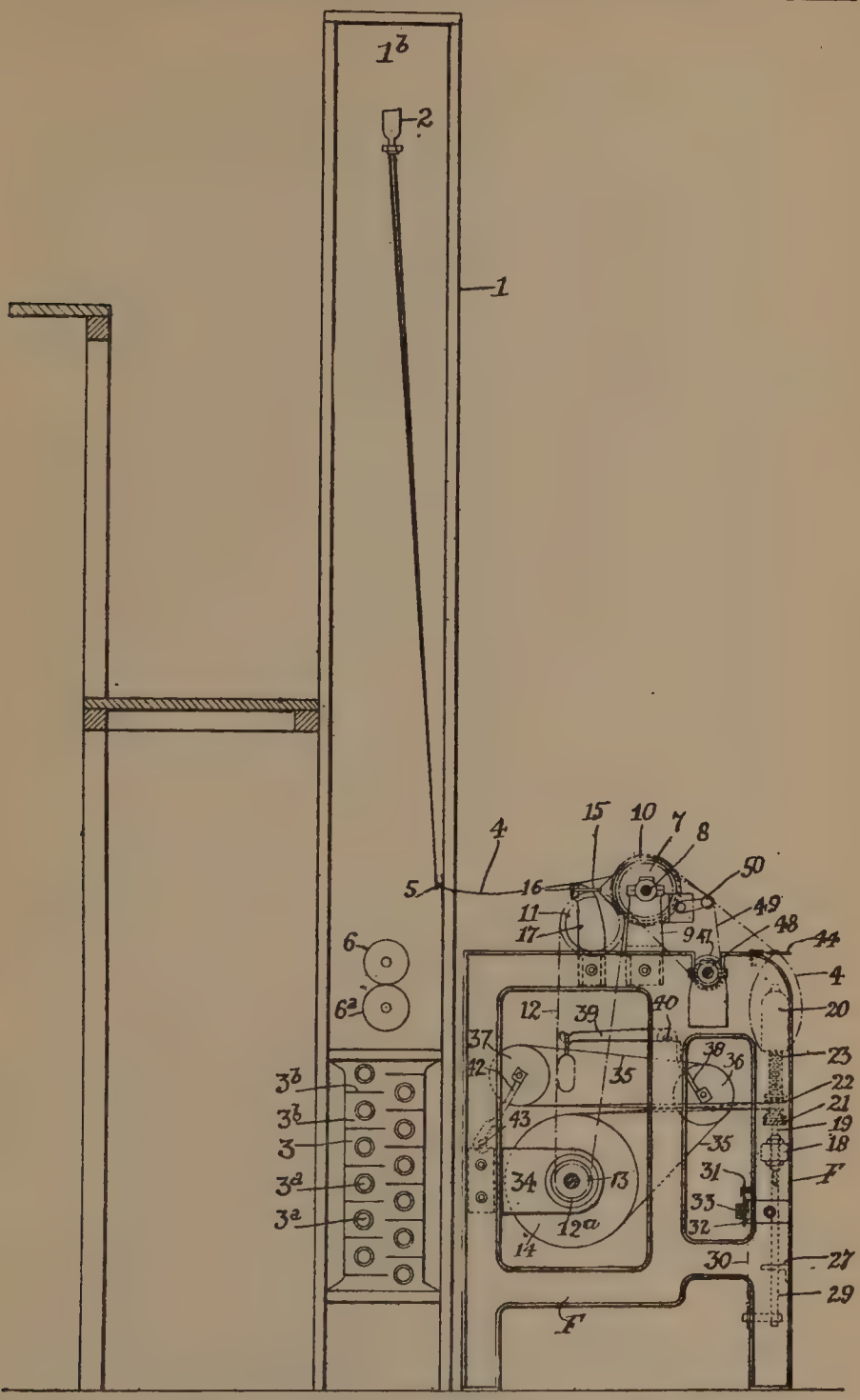

FIG. 35B.—Side Elevation of Dry-spinning Machine with Cap-spinning Collecting Device.

(*English Patent* 198,023.)

(2) MILES. English Patent 19,330/1905.
(3) CLÉMENT, RIVIÈRE and COURTAULDS. English Patents 224,404 ; 224,405.
COURTAULDS and HEGAN. English Patent 229,075.
(4) BAYER. English Patents 219,333 ; 233,342.
(5) DREYFUS. English Patents 182,166 ; 210,108 ; 217,287.
BRITISH CELLULOSE and ROY. English Patent 165,519.
(6) BRITISH CELLULOSE, PALMER and WHITEHEAD. English Patent 198,023.
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BRITISH CELLULOSE, BRIGGS and YORKE. English Patent 203,092.

CHAPTER IX

MISCELLANEOUS PROCESSES

THE processes so far described are those which have survived the test of time and become established on a production basis. There are, however, several processes of chemical interest which initially appeared promising but have failed to realise expectations. There are also certain solutions of organic compounds which were suggested by the discoverers for producing artificial threads, and some of these at the present time are being tested on a small scale. Of the former class may be mentioned the production of artificial threads from aqueous solutions of gelatine and from solutions of cellulose in zinc chloride. In the latter class are the cellulose ethers (*e.g.*, ethyl cellulose), solutions of cellulose in sulphocyanide salts and solutions of casein.

Gelatine or Vandura Silk (1).

In 1894 Millar patented the production of artificial threads from gelatine solutions, and fixing them by means of tanning agents, such as the alums, potassium dichromate, tannic acid and formaldehyde. A company was started to use this process but had a short existence, as the artificial silk was not strong enough for textile requirements.

Zinc Chloride Process (2).

The spinning of cellulose dissolved in zinc chloride solutions has been used to some extent in the production of threads for electric-lamp filaments, but the artificial-silk threads made by this process have not been a success, partly because the zinc chloride has a strong hydrolytic action on the cellulose dissolved in it, and this gives rise to weak threads.

Cellulose-ether Process (3).

The production of cellulose ethers by the action of alkyl sulphates on cellulose in presence of alkali has aroused considerable interest, as the products have a very wide solubility range, according to the number of alkyl (generally methyl or ethyl groups) groups introduced into the cellulose molecule. Solutions of the ether in organic solvents can be spun by the wet or dry spinning method. The large scale production of the cellulose ethyl-ether silk is in process of development, but the properties of this artificial silk are as yet but little known. It is, however, not unlikely that developments of this process will be seen in the future, provided that the cost of preparing the ether is commensurable with that of producing other artificial silks. The final thread would be similar to that produced by the acetate process, in that it would still be a compound of cellulose.

Cellulose and Sulphocyanide Solutions (4).

The action of salts of sulphocyanic acid on cellulose has been known for some time, and attention was recently drawn to the possibility of making cellulose solutions in this way that would be suitable for producing films and filaments. It does not, however, at present seem very likely that this method of dispersing cellulose in salt solutions is likely to be of much value for artificial-silk production.

Solutions of Casein (5).

The production of threads from alkaline solutions of casein (12·5% casein) by spinning into acid-alcohol solutions has been attempted, but the artificial silks produced therefrom were deficient in softness and strength, and the manufacture was not a commercial success.

From time to time other solutions of cellulose, or compounds other than those referred to, have been

suggested (*e.g.*, solutions of cellulose in caustic soda, cellulose-formate solutions, rubber solutions, cellulose-thiourethane solutions, solutions of acetates of cellulose ether (6)), but their successful exploitation is largely governed by the factor of working costs, and the equivalence or superiority of these processes, and of the artificial silks obtained to those now in use.

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Cellulose-thiourethane Solutions.
LILIENFELDT. English Patents 216,475 ; 231,806 ; 248,994.
Cellulose-ether-acetate Solutions.
COURTAULDS, GLOVER and WEYENBERGH. English Patents 241,679 ; 268,552.

CHAPTER X

PROPERTIES OF ARTIFICIAL SILK

I.—General.

THE properties of artificial silk have to be considered more in relation to the uses to which the fibre has to be put than to the actual physical and chemical properties of the regenerated cellulose or cellulose compounds of which artificial silk is composed. In other words, the textile user demands certain properties of the fibre he wishes to knit, weave or spin with other fibres. The physicist, the chemist and the engineer have therefore aimed at producing such a fibre. The result has, however, had to be in the nature of a compromise; the textile user has had to adapt his methods of working fibres to the new fibre, whilst the chemist has had to study the methods of producing a fibre with the required properties. The chief properties of the artificial silks can be conveniently classified as physical, mechanical, chemical, and colloidal.

Physical Properties.

The most important physical properties are the optical, *i.e.*, those concerned with the appearance of the finished artificial silk, such as colour and lustre. From the point of view of clothing, the thermal conductivity of artificial silk is of importance, whilst the insulating properties of the fibre find application in the electrical industry. In these respects cellulose-acetate artificial silk is superior to the other kinds, as it is a bad conductor.

Colour.—The colour of bleached artificial silks made from wood-pulp, such as viscose, is usually a very pale

cream ; the artificial silks produced from cotton have a bluish-white appearance. In some cases it is necessary to " blue " the bleached viscose silk by the use of certain dye solutions to neutralise the cream colour and obtain a purer white effect. Unbleached viscose silk has a straw-coloured appearance, and can be used when it is to be dyed dark shades, but for lighter shades the colour is too marked.

Lustre.—Artificial silks, in comparison with real silk, are characterised by their brilliant lustre. In wet-spinning processes, such as the viscose and cuprammonium, the lustre is conditioned by the initial stretching of the thread while in the gel condition. This stretching, as has already been explained, prevents the wet thread from contracting as it is dried. To a certain extent, therefore, the lustre is determined by the extent to which the thread is stretched or allowed to contract. This lustre is largely due to the unbroken surface of an almost transparent or translucent fibre. The nature of the lustre varies to a certain extent with the variety of the artificial silk. Herzog, who has investigated in great detail the lustre of artificial silks, ascribes the variations in the kind and degree of lustre to the outer and inner structure of the thread, such structure being to a large extent influenced by the nature of the process, and incidentally by the presence of gaseous and solid impurities and size of the individual filaments (1).

It is, however, important that an even lustre be maintained in manufacture. According to Hottenroth, nitrocellulose silk has a strong, glistening, metallic lustre ; cuprammonium silk, a strong glassy appearance ; viscose silk, a subdued silvery lustre ; whilst cellulose-acetate silk has a subdued glistening lustre like the nitro-cellulose variety (2). For some textile requirements this lustre of artificial silk is excessive, and recent tendency has been to modify it by variations in manufacture.

Thus, in the case of viscose, lustre can be reduced to the point of extinction, even after stretching, by leaving sulphur in the thread. The normal amount of sulphur in the spun thread can also be increased by the addition of sulphides to the viscose. Treatment with certain strengths of acids, alkalis and colloids can also effect a modification of the lustre (3).

Another method applicable to the cellulose silks, proposed by Bruckhaus, consists in the even precipitation of barium sulphate on the thread by use of suitable solutions of sulphuric acid and barium chloride. The thread is also weighted thereby (4).

The lustre of cellulose-acetate silk is completely removed by boiling water or steam, and by boiling it with solutions of certain salts and sugars. By control of the conditions, it has been found possible to vary the degree of de-lustring to any desired extent. Lustre which has been removed by treatment with boiling water can be restored by treatment with acetic acid, phenol and other organic compounds and solutions of ammonium sulphocyanide (5).

It may be of interest to point out that an optical instrument—the Goerz " glarimeter "—has recently been brought out which enables the lustre of fabrics to be compared quantitatively to an arbitrary scale.

It will thus be seen that it is possible, within limits, to reduce the lustre of the thread to specific requirements. The extent to which this has been attained can be judged by the fact that a recent writer stated that in " feel " and appearance many modern artificial silks are approaching nearer to real silk (6).

General Optical Properties.

The general optical characteristics of the different artificial silks have been closely studied by Herzog and his co-workers for a number of years (7).

Thus the refractive index of the various makes of

artificial silk has been determined and compared with other fibres :—

Fibre	μ_D Axis of thread at right angles to the plane of polarisation	μ_D Axis of thread parallel to plane of polarisation	Mean Refractive Index
Silk	1·595	1·538	1·567
Flax	1·595	1·528	1·562
Spun silk	1·581	1·542	1·562
Cotton	1·580	1·533	1·557
Wool	—	—	1·551
Nitrocellulose silk	1·548	1·518	1·532
Cuprammonium silk	1·548	1·527	1·538
Viscose silk	1·548	1·524	1·536
Cellulose-acetate silk	1·474	1·479	1·477

Herzog has also studied in detail the interference colours exhibited by artificial silks between crossed nicols. Such colours, of course, depend on the specific double refraction and the optical thickness of the fibre (8). Artificial silks also exhibit pleochroisim effects with certain dyestuffs. Recently, Faust has shown that the double refraction of artificial-silk threads is due to tension put on the thread during the process of manufacture (9). The examination of artificial silks by the X-ray spectroscope has indicated that all of them, except cellulose-acetate silk, exhibit a crystalline structure symmetrically disposed similar to that of mercerised cellulose (10). The examination of artificial silks by the ultra-microscope has also indicated that they all have a net-like structure, but they show certain definite differences among themselves (11).

The microscopic study of all the optical properties of artificial silks is of considerable importance to the manufacturer, as it enables valuable data to be accumulated which, when correlated, characterise the different methods of manufacture, and also show up variations and faults in manufacture.

Mechanical Properties.

Under the mechanical properties of the artificial silks the structure of the fibre, especially in relation to the textile properties of feel and covering power, and also its strength and elasticity, will be considered.

Specific Gravity.—The specific gravity of artificial silks is greater than that of other fibres. The following figures are given by Foltzer (12) :—

Nitrocellulose	1·52
Cuprammonium . . .	1·50
Viscose	1·50

Determinations carried out in Messrs. Courtaulds' laboratory indicated that the specific gravity of viscose silks ranged between 1·519 and 1·529 by the displacement method, and 1·494 and 1·508 by the flotation method, using organic liquids in both cases (13).

The following figures, given by Herzog, are rather higher (14) :—

Nitrocellulose (Tubize, 1922) .	1·56
,, (old) . . .	1·54
Cuprammonium (Glanzstoff, old)	1·53
,, (Bemberg, 1922)	1·53
Viscose (Elberfeldt, 1922) . .	1·53
,, (Küttner, recent) . .	1·52
Cellulose acetate (1922) . .	1·26

It may be of interest in this connection to give the specific gravities of the following natural fibres :—

Silk (boiled off) . . .	1·25
Silk (raw) . . .	1·30–1·37
Wool	1·34
Flax	1·50
Cotton	1·50

Structure.—The structure of the artificial silk fibre has already been referred to in connection with spinning and the number of filaments to a given size of thread (*cf.* Chapter IV).

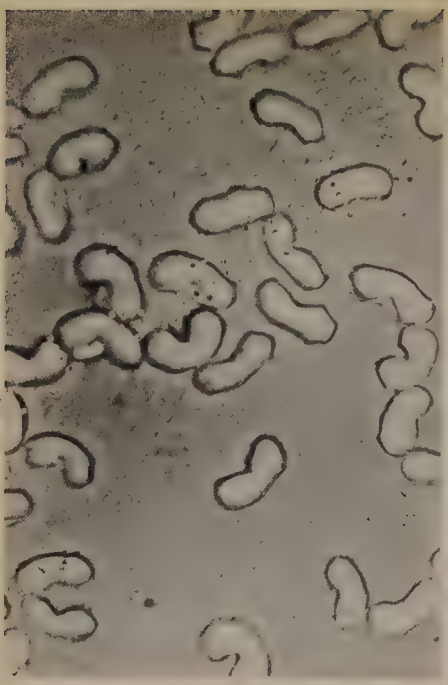

FIG. 36A.—Viscose Artificial Silk from Travis (× 260). (*King*.)

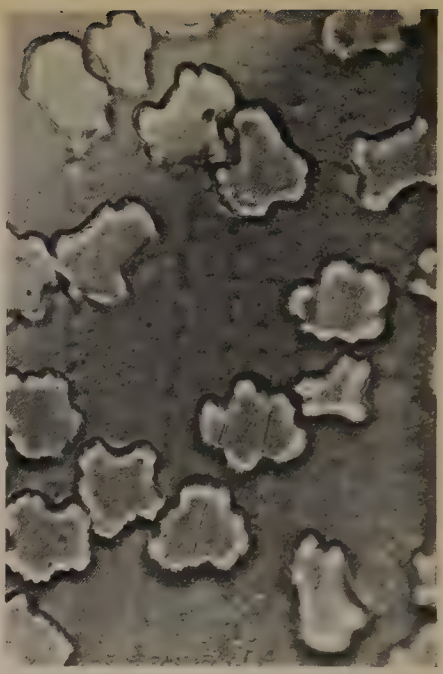

FIG. 36B.—Viscose Artificial Silk from Harbens Factory (× 260). (*King*.)

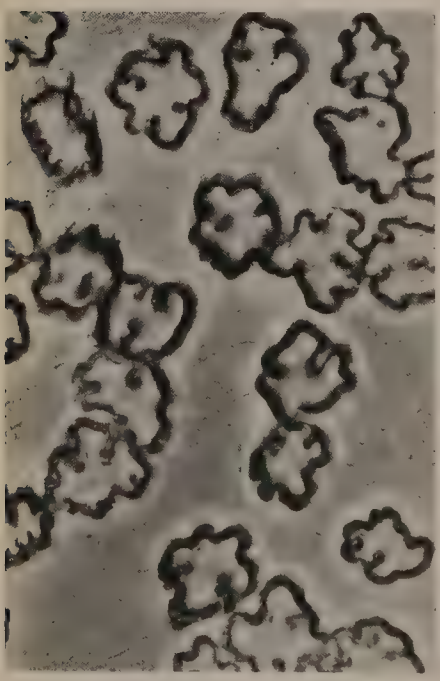

FIG. 36C.—Viscose Artificial Silk from Enka Factory (× 260). (*King*.)

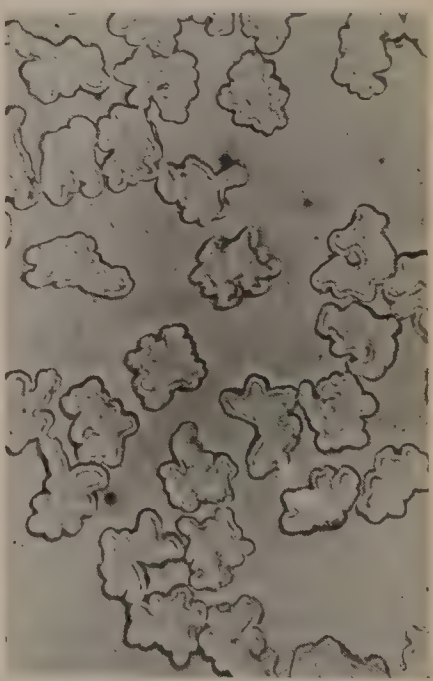

FIG. 36D.—Viscose Artificial Silk, 150 denier (× 260). (*King*.)

[*To face p.* 85.

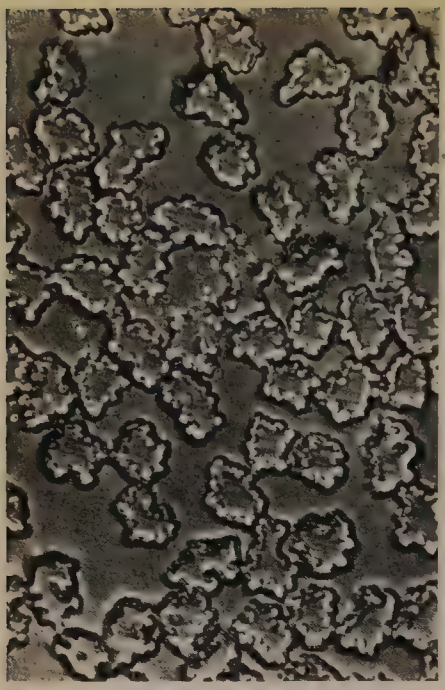

FIG. 36E.—Viscose Artificial Silk, 150 denier—made from cotton pulp (× 260).
(*King.*)

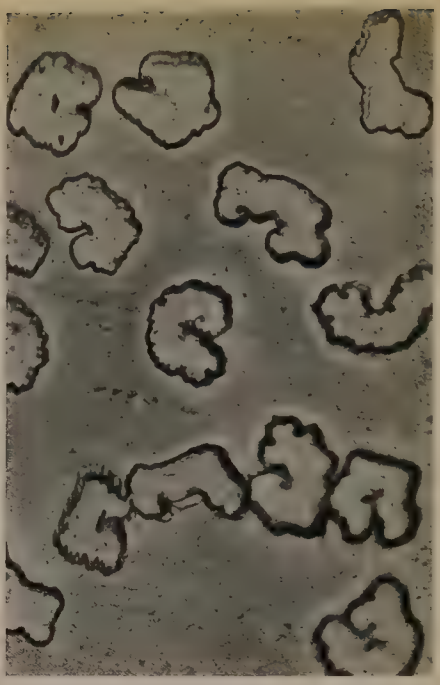

FIG. 36F.—Viscose Artificial Silk. Dyeing light shade (× 260).
(*King.*)

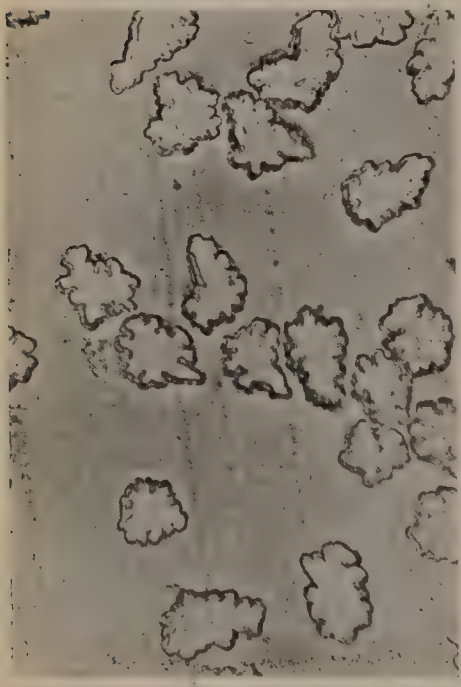

FIG. 36G.—Viscose Artificial Silk. Dyeing dark shade (× 260).
(*King.*)

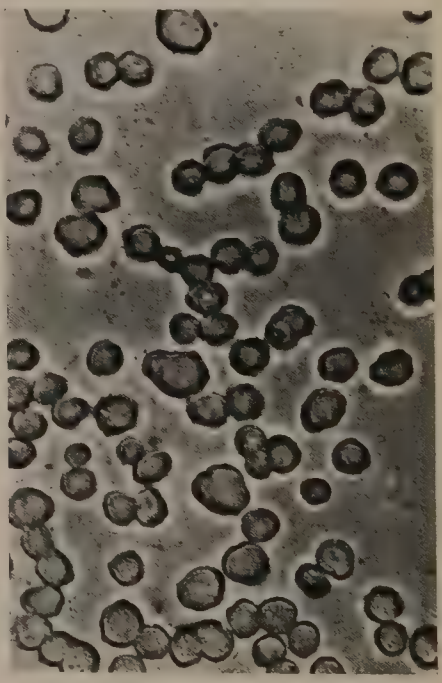

FIG. 37A.—Cuprammonium Artificial Silk, 150 denier, from Brysilka Factory (× 260).
(*King.*)

[*To face p.* 85.

Feel and Softness.—Generally speaking, the softness of the finished artificial silk largely depends on the flexibility of each filament, and the number of filaments to a given size of thread. By the stretch-spinning methods deniers equalling real silk, *i.e.*, about 0·5 denier per filament, have been produced, and sizes of 1 denier per filament are being produced in large quantities by several firms at the present time. This appears to be the practical limit of production and utilisation, as such fine fibres are very delicate and require great skill in handling and working up.

It may also be mentioned that treatment of the artificial silk to enhance the softness with soap and other chemical agents to produce a scroop, are often used, and may modify or alter the original feel (see also pp. 93, 95).

Covering Power.—Apart from the softness, one of the most important properties of all artificial silks, from the user's point of view, is their covering power (*i.e.*, covering capacity of the thread per unit weight). Now the covering power will depend on the number, breadth and bulk of the filaments in a given denier. An examination of the cross-sections of the filaments has thrown considerable light on the covering capacity of the different artificial silks. It has been found to vary very widely, depending on the process by which the thread is made, the nature of the spinning bath used, rate of setting, and the amount of stretch exerted on the thread during spinning or in the subsequent stretching process.

Figs. 36, A, B, C, D, E, F and G, are typical photomicrographs of cross-sections of viscose artificial silks produced by different factories. The smooth, rounded sections of the filaments shown in Fig. 36, A, are characteristic of a sulphuric acid-salt bath, such as the Muller bath, or a dilute sulphuric acid-ammonium sulphate bath, whilst the other sections, showing the serrated edge of the filaments, are typical of the acid-salt-glucose bath (*cf.* p. 139 of Chapter IV), most

often used in modern practice. A filament with a serrated edge is considered to have greater covering power than one with a smooth outline.

Figs. 37, A and B, show typical cross-sections of cuprammonium silk produced by the stretch-spinning process. The fineness of the 50-denier artificial silk (1 denier per filament) is clearly brought out (Fig. 37, B).

Figs. 38, A and B, are characteristic cross-sections of nitrocellulose silk spun by the dry process ; they have a kidney-shaped section and smooth outline.

Figs. 39, A, B and C, show the typical smooth, cylindrical sections of artificial silk produced by the cellulose-acetate process (15).

It will be easily realised from the different cross-sections of the various artificial silks illustrated, and also from the variations in size of the individual filaments of the same thread of artificial silk, that considerable differences in covering-power may exist between artificial silks and even between different samples from the same process. It ought also to be mentioned that the examination of the cross-sections of artificial silk fibres is a very reliable method for identifying artificial silks. Herzog has studied the same question by measuring accurately the breadth of the filaments of a large number of artificial silks, and finds that wide variations exist in the breadth of individual filaments of the same sample (16).

A considerable improvement has been effected in recent years by more careful control of the spinning jets and general standardisation of the process, so that the variations in filament size have been reduced ; but there is still room for improvement in this respect.

An interesting development in so far as covering power is concerned is the production of an aerated or tubular thread. Hitherto the greatest care has been taken to eliminate all air bubbles from the solution prior to spinning, but in spinning this new variety

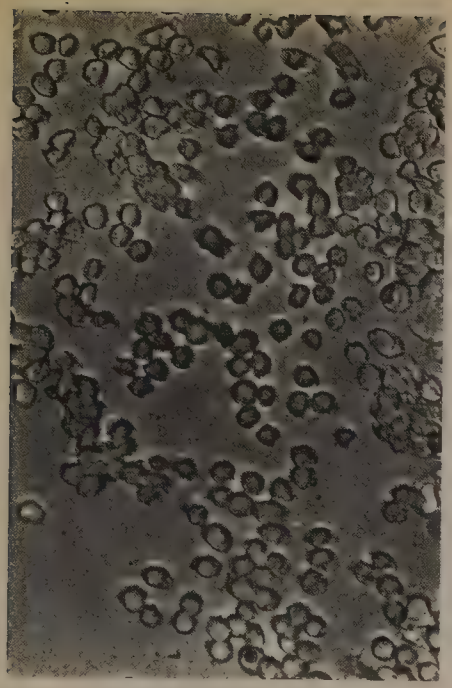

FIG. 37B.—Cuprammonium Artificial Silk (50 denier; 50 filaments) from Brysilka Factory (× 260).

(*King.*)

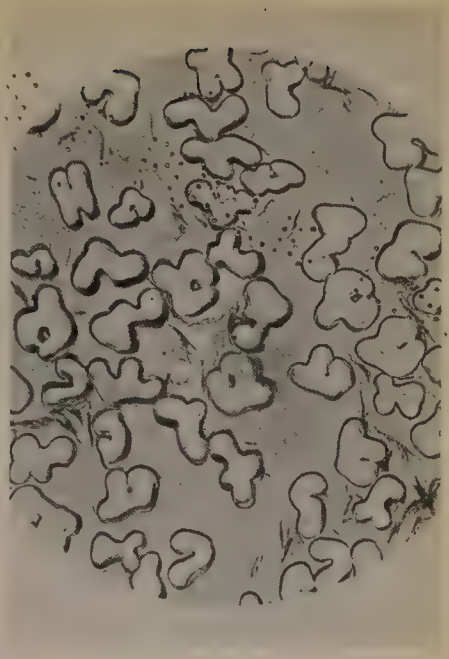

FIG. 38A.—Nitrocellulose Artficial Silk (× 200).

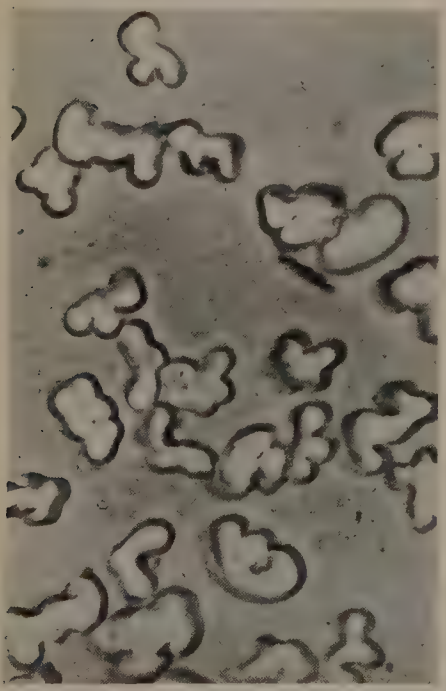

FIG. 38B.—Nitrocellulose Artificial Silk from Bulmer Rayon Factory (× 260).

(*King.*)

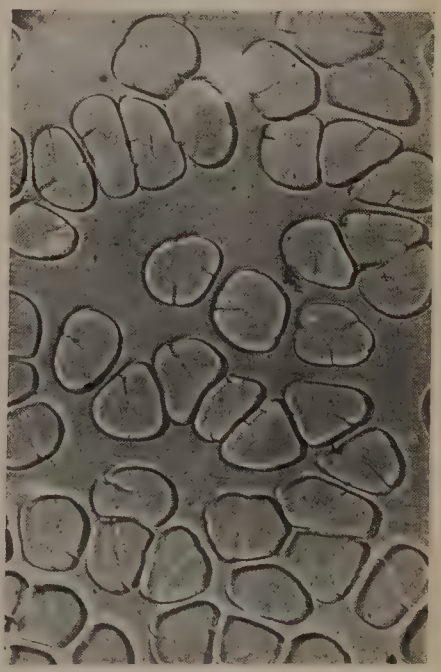

FIG. 39A.—Cellulose Acetate Artificial Silk (150 denier—Celanese) (× 195).

(*King.*)

[*To face p.* 86.

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FIG. 39B.—Cellulose Acetate Artificial Silk (Lustron) (× 260). (*King.*)

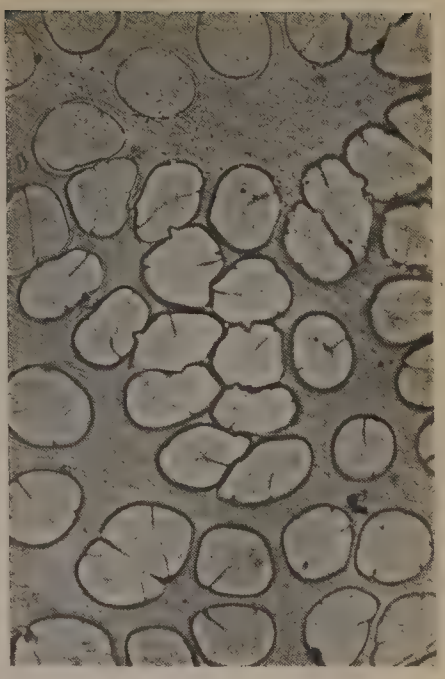

FIG. 39C.—Cellulose Acetate Artificial Silk (American Celanese) (× 260). (*King.*)

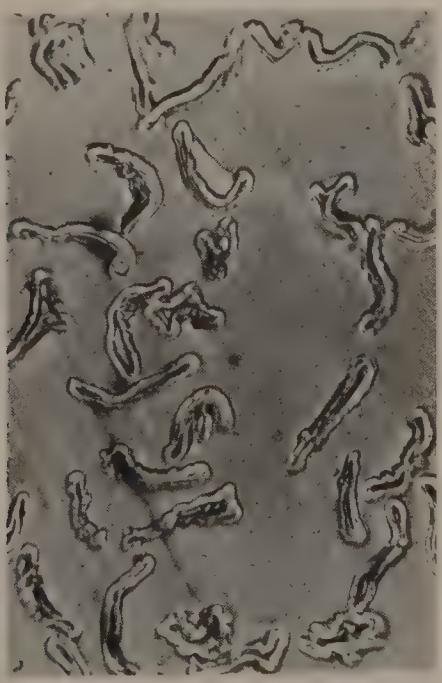

FIG. 40.—Hollow Viscose Artificial Silk (" Celta ") (× 260). (*King.*)

[*To face p.* 86.

FIG. 41.—Serimeter.

(*J. Berthaud Fils, Lyon-Villeurbanne.*)

[*To face p.* 87.

of artificial silk air is allowed to fill out each filament as produced, so that practically tubular filaments result. In the finishing process the threads are deflated. The resulting product is stated to be lighter, bulkier, warmer to wear, and to have 50% increased covering-power compared with the ordinary non-aerated artificial silk (17). Thus, for example, 100 denier of such an artificial silk goes as far as 150 denier of the ordinary product. (The method of production will be referred to in Chapter XIII.) A photomicrograph of the cross-section of the thread of an artificial silk of this kind, known as " Celta " and produced from viscose, is shown in Fig. 40.

Strength and Elasticity.

Further very important properties of a fibre are its strength and elasticity, as on these depend its value for use in weaving, spinning, knitting and in the wear of the material made from it.

In artificial-silk manufacture every endeavour has been made to increase the tenacity and elasticity, as in this respect most of the artificial silks are much inferior to real silk, especially when wet.

The determination of these quantities is carried out very simply on suitable machines, such as have been used for many years for silk-testing (Serimeters).

Two typical machines are illustrated in Figs. 41 and 42. In the serimeter shown (Fig. 41), a thread is fixed between two screws 50 cm. apart and when the catch is released, a pull is exerted automatically by the descent of the carriage by gravity. The weight at which the thread breaks and the elongation of the thread at break are recorded on suitably arranged dials. In the other type the pull on the thread is exerted by the descent of a piston in a cylinder of oil. A stress-strain diagram recorder can also be attached to these machines (see Fig. 42, facing p. 88).

The results obtained are expressed in grams per denier or tenacity and percentage elongation.

In the following table are given the wet and dry tenacities and elongations of a number of recent samples of various deniers of artificial silks, corrected to 66% relative humidity and 59° F. The determinations were carried out by Mr. P. E. King, A.I.C., of Leeds University, who has communicated the following account of the method adopted for carrying out the tests :—

The samples of artificial silks are conditioned in an atmosphere of 70% humidity and at a temperature of 70° F. for at least thirty hours before testing. The skeins are cut at one place, tied up, and twenty threads are taken out from various places. The length tested is 18 inches. It has been found that when twenty threads are selected from a skein in this manner, the mean value is as accurate as by winding from a skein and taking a larger number of test pieces.

The Baer single-thread testing machine was used ; this machine works on a similar principle to the English machine illustrated in Fig. 42. The speed of fall of the machine was adjusted to 1 foot per minute.

The wet tenacities were determined by immersing the whole length in water for thirty seconds in the case of viscose, cuprammonium and nitrocellulose artificial silks, and for fifteen minutes in the case of the cellulose-acetate artificial silks.

Wetting the long length of the thread is necessary when the wet elongation is required, but for the wet tenacity it is sufficiently accurate to wet about 4 inches in the middle of the thread and then determine the tenacity.

For comparison, the figures for natural silk have been inserted in the table. The great reduction in the tenacity of the artificial silks on wetting is obvious. The wet tenacity seldom attains 50% of the dry tenacity except in the case of cellulose-acetate silk, which has a greater resistance to water.

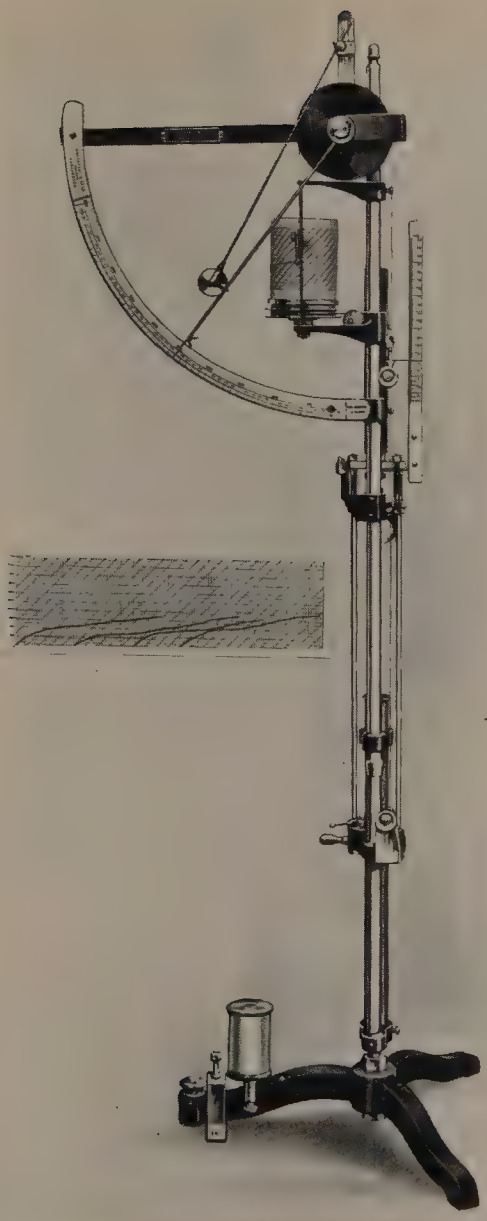

FIG. 42.—Single-thread Testing Machine, with Stress-strain Diagram Recorder.

(Goodbrand & Co., Ltd., Stalybridge.)

[*To face p.* 88.

	Tenacity Grams per denier		Elongation	
	Dry	Wet	Dry	Wet
English Viscose			%	%
50 denier . .	1·46	0·82	17·3	18·8
50 ,, . .	1·58	0·86	21·9	23·3
75 ,, . .	1·20	0·63	27·3	30·8
75 ,, . .	1·38	0·78	27·6	38·3
100 ,, . .	1·22	0·60	27·2	33·1
100 ,, . .	1·41	0·73	24·4	32·4
150 ,, . .	1·27	0·57	24·5	30·3
150 ,, . .	1·40	0·64	22·5	28·1
150 ,, . .	1·51	0·71	20·1	24·4
170 ,, . .	1·55	0·64	24·4	31·4
250 ,, . .	1·28	0·55	21·6	25·9
250 ,, . .	1·57	0·68	23·9	34·3
300 ,, . .	1·18	0·48	23·2	27·0
Foreign Viscose				
100 denier . .	1·13	0·52	15·7	15·5
100 ,, . .	1·20	0·51	18·9	21·3
100 ,, . .	1·25	0·77	23·3	29·7
150 ,, . .	1·34	0·64	22·2	29·4
200 ,, . .	1·31	0·59	19·4	23·5
250 ,, . .	1·48	0·65	19·5	23·3
Celta				
100 denier . .	1·01	0·44	18·5	16·4
150 ,, . .	1·08	0·50	16·9	18·2
Cuprammonium (fine filament)				
50 denier . .	1·22	0·65	12·4	12·3
75 ,, . .	1·60	0·83	10·0	10·6
75 ,, . .	1·50	0·89	10·1	11·9
150 ,, . .	1·21	0·51	10·1	8·8
200 ,, . .	1·47	0·73	10·1	11·9

	Tenacity Grams per dernier		Elongation	
	Dry	Wet	Dry	Wet
Nitrocellulose				
200 denier . .	1·27	0·50	15·1	11·8
Cellulose Acetate				
45 denier . .	1·17	0·74	19·7	—
75 ,, . .	1·18	0·65	18·9	—
120 ,, . .	1·13	0·65	25·9	30·3
150 ,, . .	1·18	0·69	23·8	30·6
190 ,, . .	1·20	0·68	25·5	32·9
300 ,, . .	1·21	0·67	26·7	35·3
Natural Silk . . .	2·5	2·0	21·0	

The results may be expressed in another form by showing the wet strength as a percentage of the dry strength. The following average figures are given by Obermiller and Goertz (18) from the results of a number of tests :—

	$\frac{\text{Wet tenacity} \times 100}{\text{Dry tenacity}}$
Viscose	45–55
Cuprammonium	50–60
Nitrocellulose	30–40
Cellulose acetate	65–70
Natural silk	75–80

The low results for the elongation of cuprammonium silks (fine filaments) indicate the extent to which the thread has been stretched in spinning, and lend support to the view expressed some years ago by Dreaper and Davis that each individual filament has a skin, and that the strength of this skin and the relation of the surface of this skin to the cross-sectional area determine the strength and elasticity, the latter being least when the proportion of skin is greatest (19).

The figures for elongation represent the maximum stretch of the thread at the breaking-point. It should, however, be pointed out that the actual elasticity of the

thread is considerably less than this figure. Lack of sufficient elasticity is one of the great disadvantages of artificial silks in winding and weaving. When tension is applied to the thread it resists strongly up to half its breaking strength, the elongation being quite small; but with further tension the increase in elongation is much more rapid. Therefore, if in winding or weaving too great a tension is applied to the thread, 150 denier may be reduced to 130 denier. This applies to an even greater extent when the thread is wet or damp (20).

Chemical and Colloidal Properties.

The behaviour of cellulose, whether in the form of wood-pulp, cotton or artificial silk, towards chemical reagents, is only beginning to be understood, as knowledge of the colloidal nature of cellulose (and its compounds) is being extended. In the artificial-silk industry the action of water, dye, salt, soap and bleach solutions, alkalis and acids present problems of practical importance. Such reagents have been used in the textile industry for many years, but unfortunate results often attended their use before the properties of artificial silk were properly understood.

The behaviour of the various artificial silks towards such reagents will therefore be briefly discussed. Dyeing will be dealt with in Chapter XI.

Water.—The average moisture content of viscose, cuprammonium and nitrocellulose artificial silks ranges between 11% and 13%, depending on the humidity. Cellulose-acetate artificial silk has a lower moisture content, usually from 3–6%, and is less affected by alterations in the humidity.

The U.S.A. Customs specifies the following figures for regain in moisture of the dried artificial silks at 70° F. and 65% relative humidity (21).

Viscose, Nitrocellulose, Cuprammonium.	14% of the dry weight.
Cellulose acetate .	6·5% of the dry weight.

The exact nature of the affinity of cellulose for water is not known, but it is to be noted that the attraction for water increases as the cellulose is broken down, unless it is converted into a compound, such as the acetate. Beyond swelling the fibres and rendering them more tender, excess of water (hot or cold) has little effect, except in the case of cellulose acetate, when boiling water tends to destroy the lustre unless protective salts are present in solution.

Alkaline Solutions.—In many textile factories the woven fabric is scoured by means of boiling alkaline solutions. Such solutions have a considerable softening action on most of the artificial silks, rendering them particularly tender and liable to damage. In such solutions, therefore, they must be handled very carefully.

In the case of cellulose-acetate silk such treatment entirely destroys the lustre and hydrolyses the ester unless certain salts, organic compounds, or protective colloids such as sodium chloride, sodium sulphate or ammonium sulphate, or glucose are present (22).

On the other hand, it has been found that strong caustic alkali of mercerising strength has little or no action on cellulose-acetate silk at moderate temperatures for short periods, so that mixtures of cotton and cellulose acetate can be treated together in such liquors in order to mercerise the cotton (23).

Acids.—Dilute acid solutions are used as souring baths after alkaline or bleach treatments and have no deleterious effect on the artificial silks, provided the acid is completely washed out of the fibre prior to drying. It has been claimed that by leaving in a small percentage of sulphuric acid (0·22–0·16%) the strength of the thread is increased by 9–10% (24). If acids, inorganic or organic, are left in the thread it becomes weaker and more brittle, probably owing to the formation of hydro-cellulose ; organic acids, *e.g.*, lactic acid, are least harmful in this respect (25). This effect was by no means uncommon in the early days of the

production of artificial silk by the nitrocellulose process, owing to the non-removal of certain sulphuric acid compounds of cellulose which were gradually hydrolysed and gave rise to free sulphuric acid (26).

Stronger acids can exert a mercerising and parchmentising action, but their application in this connection for special effects is limited (27). Certain organic acids are, however, used for the production of the scrooping effect on artificial silks.

Scrooping.—The scrooping of artificial silk has already been referred to in connection with the feel (see p. 85). According to Matthews (28), the scroop of real silk does not appear to be an inherent property, but is produced by treatment with dilute acids ; it can also be produced on mercerised cotton and wool. The scrooping of artificial silks is usually carried out after dyeing, and is effected by treating the material first in a warm soap bath (0·5%) and then, after hydro-extracting for twenty to thirty minutes, in a cold acid-bath consisting of tartaric or formic (or acetic) acid, or a mixture of the two. The artificial silk is then dried without previous washing with water. The strength of the acid bath can vary between 0·1–0·8%, according to the degree of scroop required.

Salt Solutions.—The adsorptive power of artificial silk for rare earths is of some importance in connection with the manufacture of incandescent mantles, as such mantles are tougher and more elastic, but the adsorption coefficients are somewhat lower than those made from natural fibres.

In the manufacture of incandescent gas mantles from artificial silk to-day the collodion treatment of the impregnated and washed mantle has been dispensed with. Such mantles are stated to be harder and stronger than those manufactured from ramie (29).

An interesting application of the action of chemicals on artificial silks has recently been patented. Artificial silks are first subjected to the action of acids, alkalies, or strong salt solutions, and then treated with roughen-

ing agents such as talc or cement, or oxides are precipitated on the surface. By this means a rough surface is claimed to be obtained, so that the adhesive and intertwining properties of the thread are considerably increased, thereby increasing their wearing value, especially in combination with other fibres (30).

Colloidal Solutions.—(1) *Sizing.*—As with other fibres, the sizing of artificial-silk yarn is carried out very extensively, but special sizes have had to be selected. The object of sizing is to increase the tenacity of the thread and its resistance to friction in weaving, and to lay the loose filaments (31). Ordinary starch, which is used for many other fibres, is not suitable, because it contracts too much on drying, and so reduces the elasticity which in the case of artificial silk is already low (31). Dextrin solutions are found to be more suitable when mixed with Turkon oil.

Gelatine is largely used for sizing, a 1–2% solution containing small amounts of Turkon oil being used ; glycerol, gum arabic, and gum tragacanth are also used. More recently " Rayonal " has been used very successfully. This is chemically-treated starch (soluble starch type). A 1% solution is thin like water, clear, gives a transparent film, and tends to help the formation of a rounded thread (32).

Various other mixtures have been suggested from time to time, such as waxes, fatty acids, oils and aqueous emulsions of the same (33).

Recently, in America, the practice of applying certain oils to the artificial silk has been adopted to keep out moisture, prevent rubbing of the threads, and render them more pliable. Various mixtures of mineral and vegetable oils have been tried (32).

Special sizes in organic solvents have been suggested for use with cellulose-acetate silk ; they consist of mixtures of metallic resinates and oleates, lard, and a solvent such as benzol or xylol. In some cases gum mastic or dammar resin may be added. Such a size is usually

applied directly to the thread as it is being wound on to a bobbin from the spinning machine (34).

(2) *Soaping*.—The soaping of artificial silk is frequently carried out either as a finishing treatment to obtain softness of feel prior to bleaching treatment, or during or after dyeing to increase fastness of dyeing.

The commonest soaps used for this purpose are Marseilles soap (olive oil soap), Monopole soap,* and Turkey-red oil preparations. Soaping may be carried out at 50°–60° C., or even at the boiling-point for two hours or less with solutions of about 0·5–1% strength. Turkey-red oils are also used as dispersing media for dyestuffs; they are used in dyeing cellulose-acetate artificial silk (see p. 108).

In the case of cellulose-acetate silk, treatment with boiling soap solutions, as with other boiling solutions, destroys its lustre; but this can be overcome by adding potassium salts to the soap solutions, *e.g.*, potassium chloride or acetate (35).

Bleach Solutions.—In order to obtain the pure white colour desired in artificial silk fibres or fabrics, it is necessary to treat with bleaching solutions (see pp. 9, 51). The action of such solutions is to oxidise the colouring matter. Unfortunately all oxidising reagents act on cellulose as well, and produce oxycellulose, which is weaker than the original cellulose. This is shown in the case of the artificial silks by a reduction in the strength of the thread when it is overbleached. Consequently all bleaching operations have to be carried out under very carefully controlled conditions so that the oxidising effect on the cellulose is reduced to a minimum.

Action of Formaldehyde.—Mention has already been made of the action of water on the artificial silks in reducing their strengths, and the figures given on p. 90 indicate the very considerable reduction in the tensile strength of the material when wet. It is, therefore,

* Patent name for a product obtained by sulphonation of linseed oil.

not surprising to find that attempts have been made to overcome this great defect. The most successful has been that proposed by Eschalier, in which the artificial silk is treated with formaldehyde solution in presence of a condensing agent, such as an acid (acetic or lactic), and then dried at a raised temperature (sthenosing).

Under these conditions a condensation compound of cellulose-formaldehyde is formed which is resistant to water. The wet tenacity of such a treated thread shows little reduction on the dry tenacity, but the elongation is decreased. Moreover, the dyeing properties of artificial silk treated by this process are considerably altered (36).

A recent writer has stated that he has successfully applied a modification of this process on a large scale, but it has not been generally adopted in the industry (37).

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CHAPTER XI

PROPERTIES OF ARTIFICIAL SILK

II.—Dyeing.

When the use of artificial silk first came into prominence in the textile industry, the difficulties that were likely to be encountered in dyeing were not properly appreciated, and consequently unsatisfactory results for a time aroused considerable prejudice against its use. Moreover, owing to the decrease in strength of all artificial silk on wetting, it had to be handled with considerably greater care than had been customary in dyeing other fibres.

The artificial silks, such as those made by the nitrocellulose, cuprammonium and viscose processes, being regenerated celluloses, were naturally considered to have similar affinity for dyestuffs as for cotton, and generally speaking, this supposition was correct. But the chemical treatment through which the cellulose raw material passes, and the mechanical treatment of the spun thread, modify the cellulose and usually increase to different extents the affinity for direct and basic dyestuffs as compared with cotton. Moreover, as the spinning of the thread and the twisting into yarn constitute one continuous operation, the mixing of threads from several spinning batches is precluded, so that the blending of different qualities of materials, normally associated with the spinning of all natural fibres, cannot be carried out. Consequently, uneven dyeing effects are one of the most serious defects of artificial silks.

Unevenness in dyeing will show up as " bars " or " shiners " (*i.e.*, stripes or markings more heavily or more lightly dyed than other portions) when the yarn is woven or knitted. By suitable selection of dyes and dyeing methods these undesirable effects

can be to a great extent mitigated, and most dye manufacturers draw attention to the tendency of certain dyestuffs for producing more even shades than others.

Thus, in the case of nitrocellulose artificial silk, differences in the dyeing behaviour of batches made by the same process have been ascribed to differences in the content of oxycellulose, and also to the percentage of nitrogen left in the thread after denitration (1).

Again, in the case of viscose artificial silk, differences in dyeing may be caused by variations in the rate of coagulation of the thread in the spinning-bath, in the age of the viscose, in the composition of the spinning-bath, by unequally sized filaments, due to incorrect holes in the jet, by tension of the thread in spinning, by excessive bleaching of the finished thread, and by unequal stretching on drying.

Similar factors in the spinning of cuprammonium artificial silk may also cause unevenness in dyeing (2). Such variations may produce differences even in the same skein, so that portions of the thread may show varying affinities for the same dyestuffs. It has even been proposed to dye the batches of artificial silk, sort them according to shade, and then remove the dye (3).

The dyeing of cellulose-acetate artificial silk involves quite a special chemical problem, as the dyeing affinity of a cellulose compound is quite different from that of a regenerated cellulose. The experience gained in the dyeing of the older artificial silks proved, however, of considerable value in the dyeing of cellulose acetate, when suitable dyes and methods of dyeing for this fibre became available. So far the output of cellulose-ether silk has been so small that the problem of dyeing it has attracted little attention, but it is not unlikely that the methods of dyeing and the classes of dyestuff used for cellulose acetate will also prove suitable for this artificial silk.

The dyeing of artificial silks of the regenerated cellulose type (nitrocellulose, cuprammonium and

viscose), will be first considered in relation to the main classes of dyestuffs, viz., Direct Cotton, Basic, Acid, Azoic, Sulphur and Vat Colours. The dyeing of cellulose-acetate silk will then be dealt with according to the special classes of dyestuff with which it can be dyed.

1.—Dyeing of Regenerated Cellulose Artificial Silk.

Direct Cotton Colours.—The affinity for direct cotton colours of cuprammonium and viscose artificial silks is about the same, though usually cuprammonium silk tends to dye more like mercerised cotton and, under the same dyeing conditions, gives deeper shades than viscose. Nitrocellulose artificial silk, on the other hand, has distinctly less affinity for the direct dyestuffs than either of the other two artificial silks mentioned.

The variations in the process which cause unevenness in dyeing have already been referred to (see p. 99), but it has also been found that certain dyestuffs have more tendency to show such unevenness than others. From this point of view, Wilson and Imison classified a large number of direct dyestuffs as even, moderately even, and uneven, and considered that to a certain extent some dyestuffs were especially sensitive in this respect (4). Whittaker has also investigated the factors causing unevenness in dyeing and has devised a test for ascertaining the degree of evenness for a large number of direct dyestuffs on artificial silks. He has allocated to the dyestuffs a number indicating whether it dyes more or less evenly or unevenly (5). Wilson's pioneer researches on this question led to extensive investigation being carried out by the dye manufacturers with the object of making dyes which were less sensitive to small variations in the artificial silks. The results of the work carried out have shown that there is a certain connection between the constitution of a dyestuff and its dyeing properties on viscose silk ; a special series of dyestuffs (" Icyl ") has recently

been put on the market possessing special even dyeing properties for viscose silk (6).

The usual conditions of dyeing artificial silk with direct cotton dyestuffs as recommended by dyestuff manufacturers are given on p. 103.

Basic Dyestuffs.—Nitrocellulose artificial silk has a greater affinity for basic dyestuffs than either viscose or cuprammonium silk. Moreover, viscose silk generally dyes more deeply than cuprammonium silk under similar conditions, but the difference is not so great as that between these artificial silks and nitrocellulose silk.

Consequently, it is not surprising to find that the dyeing of nitrocellulose and even of viscose artificial silks can be carried out without a mordant for light and medium shades, whilst in the case of cuprammonium artificial silk a mordant is necessary, even for light shades. Dyeing without a mordant is, however, preferable for reasons of fastness to light and washing.

The usual conditions for dyeing these artificial silks with basic dyestuffs are as follows : The artificial silk is first wetted out at 120° F. (49° C.), and then treated in a cold bath of 5–10% acetic acid, to which the solution of the dyestuff is gradually added, the temperature being gradually raised to 120°–160° F. (49°–71° C.) within three-quarters to one hour.

When mordanting is necessary, the yarn can be treated in a bath containing 2–5% tannic acid and 0·5–1% hydrochloric acid at a temperature of 100°–120° F. (38°–49° C.) for two hours ; after hydro-extracting it is worked for twenty minutes to half an hour in a cold bath containing 1–2·5% tartar emetic, and well washed. The proportion of liquid to artificial silk is usually about 30 : 1. Dyeing is subsequently carried out as described above. Local practice may vary in regard to these conditions of mordanting and dyeing, but the above description represents typical practice.

It may be of interest to point out that attempts have recently been made to modify the dyeing properties of

Dyeing Artificial Silk with Direct Cotton Dyestuffs

(*a*) *British Dyestuffs Corporation*

Shade	Proportion of artificial silk to dye liquor	Temperature of dye bath	Duration of dyeing	Additions to dye bath
Light. .	1 : 20–30	90°–120° F. (32°–49° C.)	½–¾ hr.	1% soda and soluble oil.
Medium .	1 : 20–30	120°–150° F. (49°–65° C.)	½–¾ hr.	1–1½% soda. 5–10% Glauber's salt with or without soluble oil.
Dark . .	1 : 20–30	150°–190° F. (65°–88° C.)	½–¾ hr.	1–2% soda. 20–30% Glauber's salt or common salt.

In many cases of dyeing with direct cotton dyestuffs more level results on uneven artificial silks are obtained when these are dyed with a small amount of acetic acid in the dye bath.

(*b*) *Clayton Aniline Co., Ltd.*

Shade	Proportion of artificial silk to dye liquor	Temperature of dye bath	Duration of dyeing	Additions to dye bath
Delicate light	1 : 20–30	80°–160° F. (27°–71° C.)	½–¾ hr.	½–1% soda ash 1–2% Monopole soap.
Fuller light .	1 : 20–30	80°–160° F.	½–¾ hr.	½–1% soda ash 1–2% Monopole soap 5–10% Glauber's salt.
Medium and Dark .	1 : 20–30	80°–160° F.	½–¾ hr.	½–1% soda ash 1–2% Monopole soap. 20–40% Glauber's salt.

In the case of cuprammonium artificial silk, Glauber's salt is unnecessary for dyeing light shades, whilst the amount can be reduced for medium and dark shades.

In the case of viscose artificial silk, the temperature of the dye bath can be raised to 180° F. (82° C.).

artificial silk by special treatments. Thus it has been claimed that by the action of halogen compounds of phosphorus on viscose artificial silk the affinity for the direct cotton dyestuffs can be decreased, whilst the affinity for basic dyestuffs is increased (7). In another patent the use of acetyl chloride for completely immunising viscose artificial silk to dyeing is claimed (8).

Acid Dyestuffs.—The affinity of acid dyestuffs for artificial silks is small, and they are therefore not extensively used.

Diazotising or Azoic Colours.—The diazotising dyestuffs have also been successfully applied to artificial silks, dyeing being carried out as on cotton. Care has, however, to be exercised in using certain members of this class of dyestuffs, as with deep shades the insoluble azo dyes tend to blind or render the artificial silk quite lustreless. It has been found that this effect is due to the aggregation of the colouring matter within the fibres. It appears to be due to the azo dye, and not to the diazotised base or naphthol (9).

Sulphur Dyestuffs.—Sulphur dyestuffs are not extensively used for dyeing artificial silks, partly owing to difficulties in obtaining even shades with varying qualities of artificial silks and in matching to shade quickly. The usual method of dyeing is in presence of 5–30% Glauber's salt and soap or soluble oil at 50°–80° C. for half to three-quarters of an hour, the dyestuff solution having been previously prepared by boiling the dyestuff with a concentrated solution of sodium sulphide and 5% soda ash, calculated on the weight of artificial silk to be dyed. As the variations in evenness to dyeing of artificial silks are reduced by more and more careful control of the variable factors in manufacture, the use of these dyestuffs is likely to extend.

Vat Dyestuffs.—At the present day the extensive use of artificial silks dyed to light shades for many articles of apparel has led to a demand for colours which are very fast to light and washing.

The Indanthrene and Indigo classes of dyestuffs supplied this want, and there is to-day a very wide selection of these colours available. Dyes of the former class possess the greatest fastness to light, washing and to chlorine, whilst the latter are much more satisfactory in so far as evenness of dyeing is

DYEING ARTIFICIAL SILKS WITH VAT DYESTUFFS
TYPICAL CONDITIONS FOR A 10% SHADE

Duranthrene Colours
(*British Dyestuffs Corporation*)

Wt. of artificial silk	Proportion of artificial silk to dye bath	Temp. of dyeing	Duration of dyeing	Caustic soda (100%)	Hydrosulphite powder	Other additions
30 lb.	1 : 40	10°–120° F. (40°–50°C.)	20–30 min.	3·6 lb. (6 pints of 76° Tw.)	2½ lb.	1 – 1½ lb. soap.

Caledon Colours
(*Scottish Dyes, Ltd.*)

100 lb.	1 : 20	90°–140° F. (30°–60°C.)	¾–1 hr.	2–12 lb. according to colour (0·6 – 4 gallons 53° Tw.)	2¼ lb.	1 – 2 lb. glue after treatment with soap at 80° C.

concerned. The application of these dyestuffs consists in reducing the insoluble dye to a leuco compound and dissolving the latter in caustic soda. The yarn is dyed in this solution, and the colour is developed by air oxidation or by means of a weak bleach bath. The use of hot caustic soda and bleach solutions must be very carefully controlled, owing to the injurious effect of hot alkalis and strong bleach solutions on artificial silks (see pp. 92, 95).

The affinity of most of the vat colours for viscose artificial silk is so very great that in order to obtain level dyeing the affinity has to be controlled by one or more of the following methods :—

(1) Increasing the ratio of liquor to yarn.
(2) Reducing the amount of caustic soda in the dye bath.
(3) Adding soap to the dye bath.
(4) Re-adjusting the temperature of dyeing.
(5) Using retarding agents, such as fish glue.

The table on p. 105 shows the dyeing conditions for two typical series of vat colours, but the quantities of caustic soda and hydrosulphite (zinc powder and sodium bisulphite) depend on the shade desired and on the actual colour used ; they may be varied according to the shade required and the particular colour employed.

2.—Dyeing of Cellulose-Acetate Silk.

The methods of dyeing cellulose-acetate silk have changed very rapidly within the last few years. The difficulty of dyeing it with many of the dyestuffs used for the other artificial silks originally gave rise to the process involving the partial saponification of the cellulose-acetate thread, whereby its affinity for dyestuffs becomes similar to the other artificial silks. Although it was claimed that this method could be carefully regulated, so that a thread consisting of an outer layer of 20% of regenerated cellulose and an inner core of 65–70% of unaltered cellulose acetate could be obtained, it was found in practice that the dyeing was not even and the lustre was seriously affected ; the use of cellulose acetate offered, therefore, no advantage over the other kinds. Accordingly this process was not a success (10). Another method put forward was the dyeing of the yarn after previous treatment with strong solutions of ammonium sulphocyanide ; but this method also has not been widely

adopted (11). It has even been proposed to mix 5–20% nitrocellulose with the cellulose acetate in making up the spinning solution and denitrating the composite thread of nitrocellulose and cellulose acetate with 10–12% solution of alkaline or alkaline-earth hydrosulphides at 65° C. It is claimed that by this process a thread is produced having good affinity for acid, basic and vat dyestuffs (12).

Basic and Acid Dyestuffs.—Cellulose-acetate silk has a limited affinity for certain basic and acid dyestuffs. It can, for instance, be dyed with malachite green or brilliant green without a mordant in an acetic acid bath in the presence of sodium chloride at 70°–75° C. It can similarly be dyed with certain alizarin dyestuffs (13).

Azoic Dyestuffs.—Cellulose acetate has an affinity for organic bases (*e.g.*, disanisidine, α-naphthylamine, benzidine). Insoluble azo colours can therefore be formed on the fibre. The method of application is the reverse of that used for cotton and other artificial silks (*cf.* p. 104). The bases are applied as hydrochlorides, or from colloidal suspensions. The absorbed amine can then be diazotised on the fibre and coupled with various naphthols. The colours have poor penetration and are not very fast to rubbing or to light (14).

Ionamine Dyestuffs.—As, however, practically 90% of the colours used in dyeing artificial silks are direct cotton dyestuffs, it will be realised that the failure to dye cellulose acetate with these colours militated against its extensive use. The first advance in finding suitable dyestuffs was made by Green and Saunders, who found that ω-sulphonic acids of amino, azo- and amino-anthraquinone derivatives decomposed in water, liberating the free base (15). The free base, although insoluble, was in a form in which it was easily absorbed by the cellulose acetate. In certain cases the free amino-azo base is a dye in itself, but in other cases it can be developed by diazotising and coupling with phenols (*e.g.*, β-oxynaphthoic acid and β-naphthol). Dyeings are usually carried out at 80° C. in presence

of formic acid. This series of dyestuffs is known as the Ionamine series, but only a limited number of colours is available.

Duranol, Dispersol, Celatene and S.R.A. Dyestuffs.—The next development in the dyeing of cellulose acetate was the discovery that certain dyestuffs insoluble in water could be made soluble by treatment with Turkey-red Oil, sulphoricinoleic acid (S.R.A.—hence the name S.R.A. dyestuffs), or by colloidal grinding. This discovery resulted in many series of dyestuffs becoming available: the S.R.A. colours of the British Celanese Company, the Dispersol and Duranol colours of the British Dyestuffs Corporation, the Celatene colours of Scottish Dyes, Ltd., and the Cibacete colours of the Society of Chemical Industry, Bâle. A large number of these dyestuffs are derivatives of aminoanthraquinone, but other classes of groups have also been introduced (16). These dyestuffs are usually applied by adding the paste to the dye bath and dyeing between 45°–80° C. for twenty to thirty minutes.

Vat Dyestuffs.—The use of vat dyestuffs, such as indigo and sulphur dyestuffs, is possible with cellulose-acetate artificial silks, but care must be taken to use very little alkali and not too high a temperature in order to avoid saponification of the material of the thread and destruction of the lustre. The use of sodium phenate in place of caustic soda has been suggested (17).

Ellis, who has closely studied the problem of dyeing cellulose acetate, has stated that the substantive affinity of a dyestuff for cellulose acetate is very approximately proportional to its basicity, and hence inversely proportional to its acidity or its power of salt formation with bases (16). The SO_3H— group in the cotton and other dyestuffs exercises a restraining action, and consequently the cellulose acetate is not dyed. On the other hand, recent research has shown

that the introduction of the COOH — group gives rise to colours which will dye cellulose acetate. Other groups which increase the affinity are OH, NH_2, and NO_2 (18). The number of patents that are being put forward at the present time indicates that a considerable amount of research work is being carried out with the idea of rendering dyestuffs suitable for cellulose-acetate dyeing by the introduction of such groups as are referred to above. It is, therefore, not at all unlikely that the number of dyestuffs suitable for cellulose acetate will be largely increased in the future.

The very different dyeing properties of cellulose acetate enable very effective contrast-colour effects to be produced in fabric materials made up with the regenerated cellulose and cellulose-acetate artificial silks. The problems connected with the dyeing of mixtures of this kind with cotton, mercerised cotton, wool, etc., have been studied by dyestuff manufacturers, who now recommend methods of dyeing and dyestuffs that are suitable for the shades required.

The printing of artificial silks of the regenerated cellulose type is carried out in a similar manner to the printing of cotton, but the printing of cellulose acetate offers considerable difficulties owing to the impenetrability of the material; special methods are gradually being developed.

Generally, the selection of suitable dyestuffs for artificial silks will to a certain extent depend on the form in which the material is to be dyed and the degree of fastness desired. Most dyestuff manufacturers have studied the fastness of their dyestuffs to light and to the different reagents likely to be used on the textile, such as soap, bleach, and scrooping baths. Each firm tabulates its dyestuffs according to their fastness in this respect.

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CHAPTER XII

THE USES OF ARTIFICIAL SILK

A DESCRIPTION of the multifarious ways in which artificial silk can be worked up by itself, or in combination with other fibres, falls outside the scope of this volume. At the same time, a brief review of recent developments may be of interest, especially in view of the fact that many of the new factories producing artificial-silk yarn do not work up their own yarn, but serve mainly as feeders to the textile industry.

It is difficult to realise to-day that in the early days of artificial-silk production in this country it was extremely difficult to get the textile industry to take up the new fibre. Thus, when it was suggested to the knitting firms that they might try and manufacture artificial-silk stockings, hardly any of them would listen to the proposal, even if the yarn were supplied free to them for experimental purposes. Finally, a well-known Leek firm agreed to try, and eventually became the first maker of artificial-silk stockings (1). Nothing succeeds like success, and it was not long after this that the majority of the hosiery firms were eager to try the new yarn.

Statistics of the uses to which artificial silk is put are not easy to obtain, but the figures on p. 112 for this country, the United States, and Germany are of some interest as indicating the diverse uses to which artificial silk is being put to-day (2).

Such figures naturally vary from year to year, according to the demands of fashion, and as new ways are found of working up the different yarns and combining them with the older fibres.

The rapid progress that is being made in this latter respect has been demonstrated at the recent exhibitions

of artificial-silk products held in London and the provinces, and there is ample evidence that British textile designers in this country are fully maintaining

PERCENTAGE OF ARTIFICIAL SILK USED IN DIFFERENT INDUSTRIES

	U.K.	U.S.A.		Germany
	1925	1914	1925	1926
Hosiery	40	47	28	46
Knitted goods (except hosiery)		3	5	
Interwoven with cotton	25	14	26	20
Interwoven with silk		12	16	16
Interwoven with wool		2	1	
Interwoven with linen	—	—	13	18
Plush	—	15	1	
Tapestry	—	2	—	
Ribbons, braids and ties, etc.	30	3	4	
Elastic webbing	1·5	—	—	
Cords	2·5	—	—	
Miscellaneous	1	2	6	

their world-wide reputation in the case of the new fibre.

A brief survey of the chief uses of artificial silk will suffice to show the part it has come to play in modern life.

Hosiery.

It is related that a traveller, on his return to this country from the East after several years' absence, stated that what struck him most was the wonderful display of " silk " stockings in the street. Apart from the change in feminine fashions whereby the long skirt of the nineteenth century has disappeared, the use of bright and lustrous materials, such as silk, was largely limited owing to the cost of the product ; but with the introduction of artificial silk for hosiery, such articles came within the reach of the majority of the

population (male and female). Such a state of affairs is not confined to this country, but is now almost world-wide. When artificial silk was first used for hosiery it was found to have certain drawbacks, such as " laddering," which was partly due to its lack of elasticity and sensitiveness to moisture and friction. Further, the excessive lustre was considered too showy. At the present time, as has already been indicated, processes are in use whereby the lustre can be suitably modified to the purpose required. The strength of the product has been increased by the production of a " plated " article, in which wool or cotton is used on the inside of the artificial silk. This has also the advantage of being warmer for wear (3).

Knitted Goods.

Besides hosiery, there are very large quantities of knitted fabrics now being produced from artificial silk, such as stockinette, Milanese fabrics and tricots, which are made into dresses, underwear, ties, etc. (4). The production of fine denier yarns and improved methods of knitting them have largely helped in this respect.

The application of artificial silk to the production of laces and curtains has also been developing, and very fine effects can be produced in such goods as bed-spreads, chair backs, cushion covers, duchesse sets and fancy tablecloths.

Artificial silk also has very largely replaced cotton in the manufacture of elastic webs and braids.

The use of cellulose-acetate artificial silk in combination with other artificial silks has also enabled diverse colour effects to be produced owing to the difference in dyeing properties.

Artificial Silk and Cotton.

Although artificial silk is mainly used in the manufacture of the products referred to in the previous paragraph, mixtures with cotton or other fibres may

be utilised where strength or contrast effects are desired. There is now a very wide range in woven fabrics of cotton and artificial silk, which may contain percentages of artificial silk ranging from 5–60%. Thus we have cotton coatings, Bedford cords, cambric shirtings, lingerie fabrics, cotton marocains, poplins, sateens, blouse and dress fabrics, voiles, mock voiles, and many others too numerous to mention.

Artificial Silk and Wool.

The lustre, brightness, and sheen of artificial silk enable it to supplement the properties of wool, such as warmth, curl and roughness of the fibre, so that many mixtures of these two fibres enable fabrics to be produced which have advantages over either. Covert coatings, gabardines, linings and special cloths for the East are being made in increasing quantities. As the dyeing properties of the artificial silks are becoming better known, designs are becoming more ambitious so as to obtain the maximum effects.

Artificial Silk and Silk.

The fine-denier artificial-silk yarns now on the market are proving more satisfactory for mixing with real silk, and mixed fabrics are being produced with very pleasing effects, thus, *e.g.*, *crêpe-de-chines* are being made from natural silk and cellulose-acetate artificial silk.

Artificial Silk Cloths.

Besides the mixture referred to, it is of interest to point out that recent developments have shown that artificial-silk cloths can be produced in weaves hitherto only familiar in real silk, *e.g.*, *crêpe-de-chine*, marocain, foulard, jap, taffeta, satin, and surah (5).

Miscellaneous Uses.

Reference has been made in Chapter X to the use of artificial silk for incandescent gas mantles, and also as an insulating material in the electrical industry.

The above cursory review of the uses of artificial silk will have achieved its purpose if it indicates the enormous possibilities that lie in store for artificial silk, whether used alone or in combination with other fibres for all the purposes which the natural fibres have hitherto subserved. It will not be denied that industry and the world in general has gained in many ways by the introduction of artificial silk.

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CHAPTER XIII

PRODUCTION OF MISCELLANEOUS ARTIFICIAL FIBRES

THE methods of producing artificial fibres hitherto described have only covered the manufacture of the continuous solid fibre known as artificial silk, but there are certain special varieties of artificial fibres which are of some importance. These varieties have not as yet such an extended application as artificial silk itself; their use has to a certain extent depended on the vagaries of fashion and the ingenuity of manufacturers in finding outlets for them.

These products will be considered under hollow filaments, staple fibre, artificial wool, monofil or artificial horsehair and artificial straw.

Hollow Filaments.

Mention has been made in Chapter X of a new variety of artificial silk possessing special advantages, in which the filaments are hollow in contrast to most of the artificial silks hitherto produced, that consist of solid filaments. The importance of de-aerating the solution prior to spinning has been referred to as applicable to all the solutions; occasional bubbles are invariably a source of trouble and cause broken filaments, and hence fluffy artificial silk. In the earlier patents for the production of hollow filaments, it was actually proposed to emulsify the solution with air or an inert gas (1). This suggestion was followed by the idea of incorporating with the solution a substance capable of producing an inert gas within the filaments on spinning. The use of alkaline carbonates, which would give rise to carbon dioxide in a warm acid spinning bath, petrol or carbon bisulphide which would be vaporised by the heat of

the spinning bath and give rise to bubbles of gas in the filaments, have been suggested, according to the solution to be spun (2).

In the case of viscose solutions sodium carbonate is generally incorporated either by adding a certain amount to the steeping soda or to the sodium hydroxide used for dissolving the cellulose xanthate. The percentage of soda in the viscose may also be correspondingly reduced. The percentage of sodium carbonate in the viscose may range from 2·5–3% (3).

The spinning bath suitable for the production of hollow threads from viscose may be the ordinary sulphuric-acid-glucose bath (see p. 39), containing a high percentage of zinc sulphate (5%), or sulphuric-sodium sulphate varying in strength with the age of the viscose (4). The degree of inflation of the thread can be controlled by adjustment of such factors as the composition of the viscose and its degree of ripening, composition of the spinning bath used, temperature of spinning, and length of immersion (4).

In another method it has been suggested that oils, fats, sodium salts of fatty acids, or metallic soaps should be dispersed in the viscose; on spinning, the free acids would be set free in the filaments and could subsequently be extracted by means of alkalis or organic solvents, whereby hollow filaments would be produced (5).

Another inventor has suggested producing air bubbles in the viscose prior to spinning by electrolysing the viscose just prior to ejection through the holes of the spinning jet. The number of bubbles can be controlled by varying the degree of electrolysis (6).

In the case of cellulose-acetate solutions, hollow threads can be produced by spinning the solution into aqueous precipitating baths, with which the solvent is miscible, using a long immersion of the thread. Thus hollow threads can be produced by spinning a 10%

cellulose-acetate solution in acetic acid, into 5% acetic acid at 25° C. at a speed of 18 metres per minute and an immersion of 100 cm. (7).

Hollow threads can also be produced by the dry spinning of cellulose acetate or nitrate solutions into a gaseous medium heated to a considerably higher temperature than the boiling-point of the solvent used (8).

Such hollow filaments require to be deflated. This can be effected by treatment with boiling water to dissolve the gas occluded and so deflate the thread, or by subjecting the threads to a vacuum (9).

The properties of such hollow threads have already been referred to in Chapter X and the considerable advantages which such artificial silk has, in some respects, over the ordinary artificial silk may doubtless lead to its more extended production in the future (10).

Staple Fibre.

In the manufacture of artificial silk there is inevitably produced a certain amount of waste. This waste has in past years had a certain limited market, having been combed and spun or worked up into other fibres (11). The amount produced was naturally kept as low as possible in the interest of efficient manufacture of the main object of production. Prior to the war, some inventors had suggested producing large quantities of short-length waste fibrous material from viscose and other cellulose solutions, but these suggestions did not lead to any extensive manufacturing developments. During the war, owing to the shortage of textile materials in Germany, the production of fibres by such a method attracted considerable attention, and very large amounts of the so-called staple fibre were produced at various factories chiefly from viscose. Such fibres were worked in with wool and cotton to a large extent. After the war, when supplies of natural fibres became more normal the use of

staple fibre diminished, as it was found more profitable to produce continuous artificial silk from the viscose solution.

The only hope of its successful production depended, therefore, on cheapening the cost of production and producing yarns with other fibres which would compete with the natural fibres and would find new applications in the textile world. In the last few years the cost of production has been lowered by improved methods, and textile manufacturers in this country have become better acquainted with the best methods of utilisation.

Staple fibre is put on the market as tufts of filaments, of length 3–4 cm. or 5–6 cm., according as it is required for mixing with cotton or wool. It may be lustreless or it may have a subdued lustre, and in some makes (*e.g.*, Sniafil) the manufacturer has succeeded in imparting to the product a definite curl or in altering the surface of the filaments by roughening it by mechanical or other means so as to enhance the spinning properties (see p. 94).

Methods of Production.—Viscose solution has been mainly used for the spinning of staple fibre owing to its cheapness, and according to some accounts the solution can be spun without ripening into a cheap acid-salt bath.

The machines used for producing staple fibre are various. Thus a large number of filaments can be spun by using a jet with a large number of holes (*e.g.*, 200 up to 1,000) and collecting the composite thread on a suitable reel. The untwisted skein thus produced is washed, desulphurised, bleached, soured and dried, and then cut up into the required staple lengths (12). The size of the individual filaments may be as low as one denier. More recently Dreaper has proposed the centrifugal spinning method for staple fibre production, using a very large centrifugal spinning box (15 inches diameter) by which the spun threads are collected as a skein (4–8 oz.) with a very low twist (0·5 turns per inch),

(Fig. 43). After the finishing treatment the skein is cut up into the required lengths (13).

An ingenious machine has lately been patented by a German firm for the production from cellulose solu-

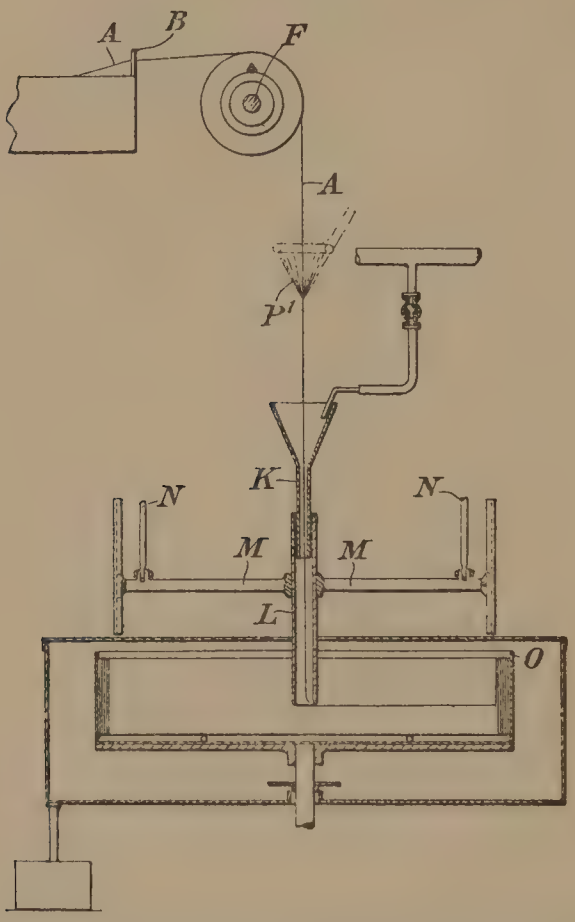

FIG. 43.—Centrifugal Spinning Machine for production of Staple Fibre.

(*English Patent* 178,481.)

tions of staple fibre which can be spun by the dry process (see Fig. 44). The machine consists of two centrifugals, an inner one *8* provided with several jets and an outer one *15*. The inner centrifugal contains the solution to be spun, and on rotation the solution is forced out through the jets *14* and solidifies as fine fila-

ments on the walls of the outer centrifugal, which has a lower peripheral speed and rotates in the opposite

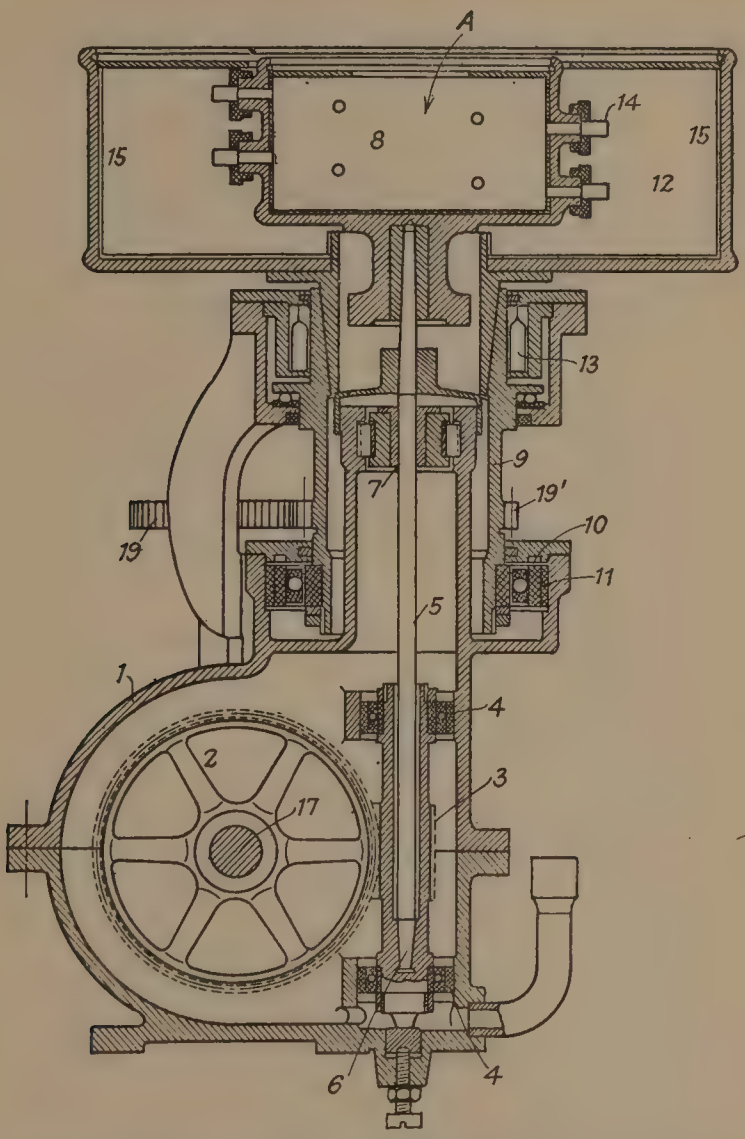

FIG. 44.—Centrifugal Spinning Machine with several jets for Staple Fibre.

(*German Patent* 400,931.)

direction. In a modification of this patent (Fig. 45), provision is made for two outer centrifugals, *13* and *14*, and one inner one, *8*, which can be raised or lowered

into one or other of the outer centrifugals while the other is being emptied. Provision is also made for

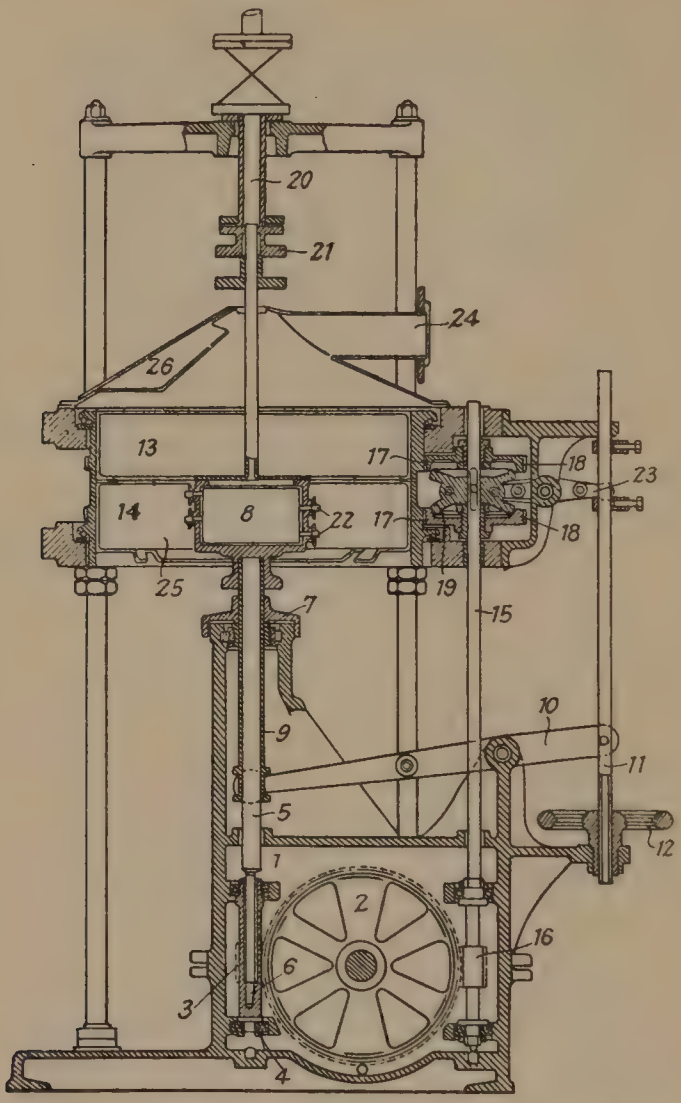

FIG. 45.—Centrifugal Spinning Machine with several jets for Staple Fibre.

(*German Patent* 401,988.)

the continuous supply of spinning solution to the inner centrifugal by a pipe 20. It will be obvious that such a machine will be able to give very large outputs of staple fibre (14).

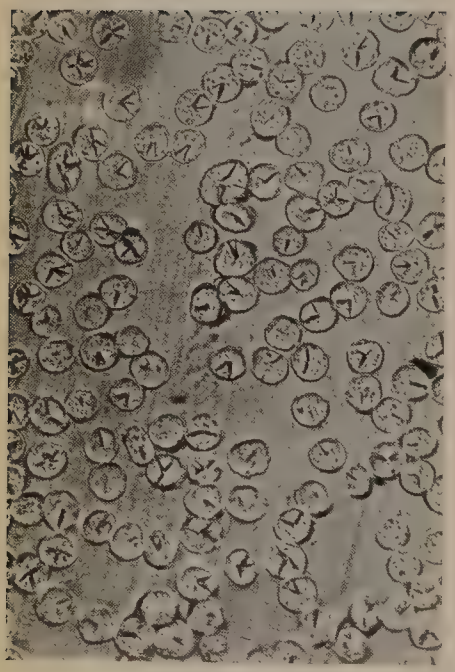

FIG. 46A.—Vistra Staple Fibre (× 260).

(*King*.)

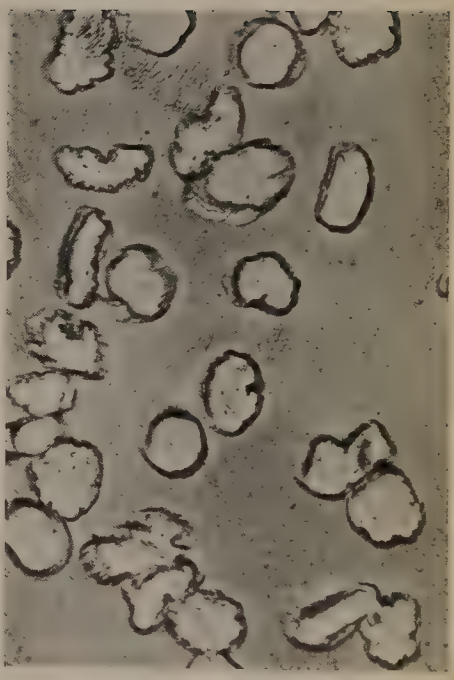

FIG. 46B.—Sniafil Staple Fibre (× 260).

(*King*.)

[*To face p.* 123.

Properties and Uses.—The properties of staple fibre are similar to those of artificial silk. Typical photomicrographs of cross sections of two well-known staple fibres—Vistra and Sniafil—are shown in Fig. 46 A and B. As referred to above, staple fibre is generally mixed with either wool or cotton and spun into a mixed thread. Such mixtures may contain from 30% up to 75% of staple fibre. In the case of wool and staple fibres, the two fibres are to a certain extent complementary, each having properties which the other lacks, the wool being soft to the touch and warm, whilst the staple fibre enhances the appearance and enables special dyeing effects to be produced. The use of staple fibre with cotton has not hitherto been so extensive as with wool (12 and 15).

It is not easy to forecast developments in the use of staple fibre, but it is not unlikely that as more applications are found for it and methods of spinning are developed, it may become a standardised product for admixing with the natural fibres.

Synthetic Wool.

Some varieties of staple fibre having little or no lustre, a roughened surface and a definite curl, all of which properties enhance their spinning value, have been termed somewhat erroneously " artificial wool." Several patents, however, have recently been taken out for producing, by the spinning of cellulose solutions, a material really approximating to wool. Pellerin (16) proposes to do this (see Fig. 47) by spinning a number of viscose threads, so that they are carried in one direction over a rotating drum *8* from the bath while still plastic; then at a certain point on the drum the direction of the threads is reversed by means of the scraper *18* and the threads are guided on to a roller which allows them to pass on to the drum *16*, and so to the collecting funnel travelling at a slower speed.

It is claimed that the effect of slowing and changing

the direction is sufficient to produce a fibrous material which has a crêpe-like appearance resembling natural wool. Other patents claim methods of altering the

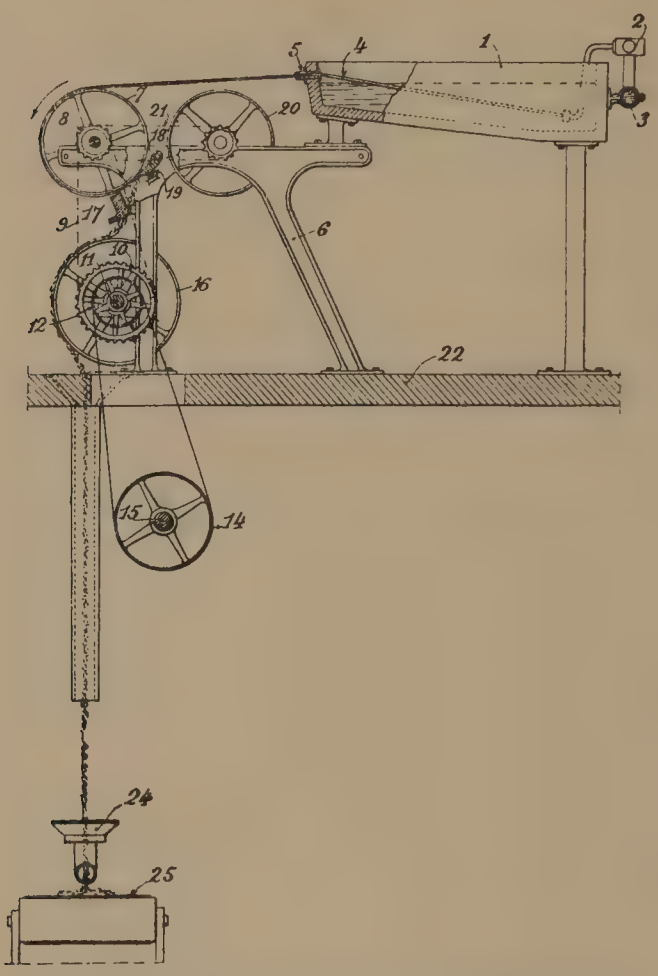

FIG. 47.—Machine for production of Synthetic Wool.
(*English Patent* 263,727.)

appearance of the staple fibre thread with a similar object in view. Such a material is stated to compare favourably in finish and appearance with the natural product, but compares unfavourably with natural wool in retaining warmth, though the production of hollow filaments (see p. 116) might offset this disadvantage.

It seems doubtful, however, whether such material is likely to be extensively used, unless it is proved to have any very special merits, or to be considerably cheaper than the natural fibre (17).

Monofil or Artificial Horsehair.

Monofil, as its name implies, is the fibre produced by spinning a single filament comprising one thread (in contrast to artificial silks in which the thread is made up of several filaments) from cellulose solutions. It has been manufactured for several years from zinc chloride, viscose or cuprammonium solutions by methods analogous to those used in the production of the artificial silks, and in sizes ranging from 30–1,000 denier singles. Zinc chloride solutions (see p. 77) were used for the production of filaments for the early manufacture of electric incandescent lamps (carbon lamps). The viscose solution is not very suitable for the production of monofil owing to the elongated nature of the cross-section. It gives a thread tending to be brittle and difficult to knot. The cuprammonium process gives a much more suitable fibre, having a rounded cross-section and greater elasticity.

Monofil is finding an extended use to-day for braids, laces, millinery and cloths, and in the finer counts for pile carpets and rugs, hair-nets and wigs (18).

Artificial Straw.

It is possible by forcing a cellulose solution through a very fine long, narrow opening to spin a flat ribbon-like material which can be finished as a bright semi-transparent material, known as artificial straw. It has been used for hat manufacture. By special jets it is possible to spin a hollow tubular material more analogous to natural straw (19). The spinning of such a material can also be arranged as an outer coating for other finished fibres. Such straw-like material, however, has so far had only a limited use, as the demand for it depends on the vagaries of fashion.

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CHAPTER XIV

THE ECONOMICS OF ARTIFICIAL SILK PRODUCTION

THE phenomenal increase in the production of artificial silk throughout the world within the last quarter of

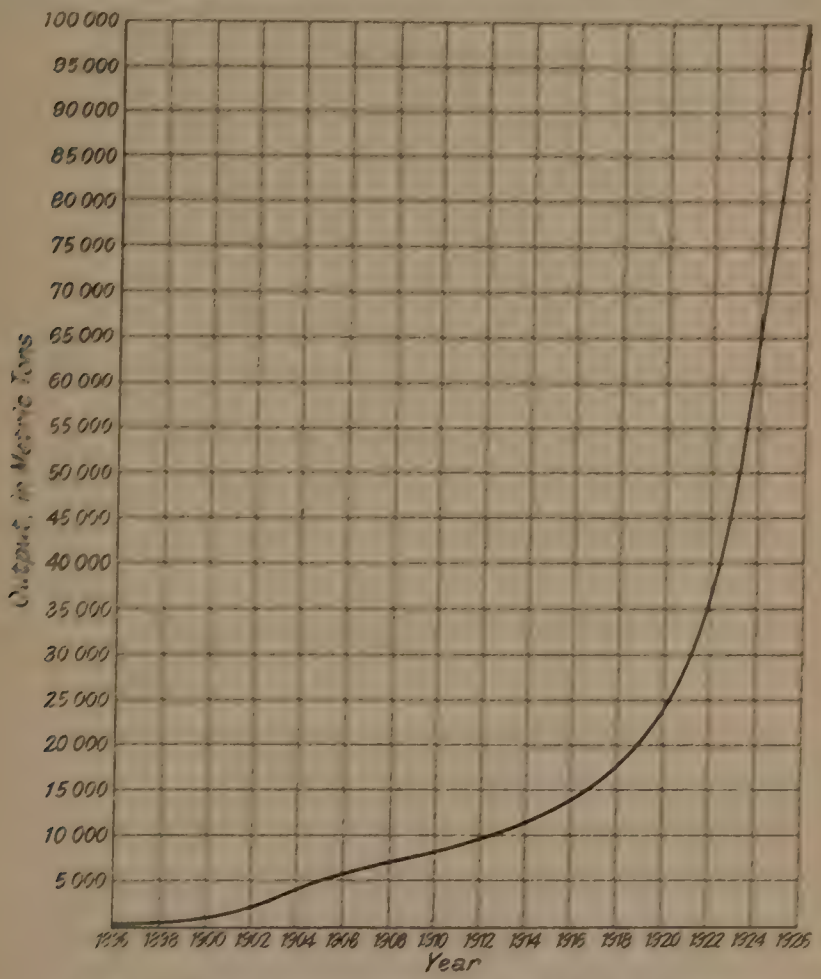

FIG. 48.—World's production of Artificial Silk, 1896–1926.

a century can best be shown by giving the figures for the world's output (1). These are tabulated below and shown graphically in Fig. 48. Certain of the earlier

figures given for output were only very approximate owing to the lack of reliable data, and must be accepted with all reserve, but the general progressive increase in the world's output of artificial silk during the period 1896–1914, and the very rapid increase during the last six years is clearly brought out.

WORLD'S OUTPUT OF ARTIFICIAL SILK *

Year	Metric Tons	Year	Metric Tons	Year	Metric Tons
1896	600	1908	7,000	1917	15,500
1900	1,000	1909	7,500	1918	16,000
1901	1,500	1910	8,000	1919	20,000
1902	2,500	1911	8,500	1920	25,000
1903	3,000	1912	9,000	1921	30,000
1904	4,000	1913	11,000	1922	35,500
1905	5,000	1914	12,000	1923	47,500
1906	6,000	1915	13,500	1924	64,000
1907	6,500	1916	15,000	1925	85,500
—	—	—	—	1926	99,500 †

The present relative importance of artificial silk in comparison with the chief natural fibres can be best shown by comparing the world's production of these fibres with artificial silk (2).

Thus the world's production in 1923 was :—

	Metric Tons
Cotton	5,227,000
Jute	1,590,000
Wool	1,364,000
Artificial silk	47,500
Natural silk	33,600
Ramie	1,130

From these figures it is seen that the world's production of artificial silk constituted only 0·6% of the whole. Although this production had practically doubled by 1926, yet even in the current year it is

* Taken from League of Nations Report on Artificial Silk, 1927.
† *Times Artificial Silk Supplement*, April 2, 1927.

unlikely that the output of artificial silk will exceed 2% of the combined output of the other fibres. It is, therefore, not surprising to find that many experts consider that the market for artificial silk has scarcely been touched; but it should be pointed out that artificial silk is not likely ever to replace the standard fibres, such as wool and cotton, for clothing purposes unless it becomes cheaper and can be produced with those properties which render wool and cotton invaluable in certain respects.

In this connection the individual production of the different countries is of interest. In the following table are given the production figures for the manufacturing countries, and Fig. 49 illustrates the same figures for the eight chief countries :—

World Production of Artificial Silk

(Taken from League of Nations Artificial Silk Report)
1913–1926

Metric Tons

Country	1913	1922	1923	1924	1925	1926*
United States	700	11,000	16,000	17,000	23,500	28,800
Italy	150	3,000	5,000	8,000	14,000	15,900
Great Britain	3,000	7,000	8,000	11,000	12,000	11,600
Germany	3,500	5,000	6,500	10,500	12,000	11,800
France	1,500	3,000	3,500	6,000	8,000	7,900
Belgium	1,300	3,000	3,500	4,000	5,000	5,900
Holland	—	1,000	1,250	2,000	4,000	6,600
Switzerland	150	750	1,500	2,000	2,500	3,600
Japan	—	100	200	600	700	2,900
Austria	700	750	750	1,000	1,500	
Poland	—	350	550	850	1,000	
Czechoslovakia	—	250	350	600	800	
Hungary	—	300	400	250	300	4,500
Spain	—	—	—	90	100	
Sweden	—	—	—	70	70	
Russia	—	—	—	40	30	
Total	11,000	35,500	47,500	64,000	85,500	99,500

* From *Times Artificial Silk Supplement*, April 2, 1927.

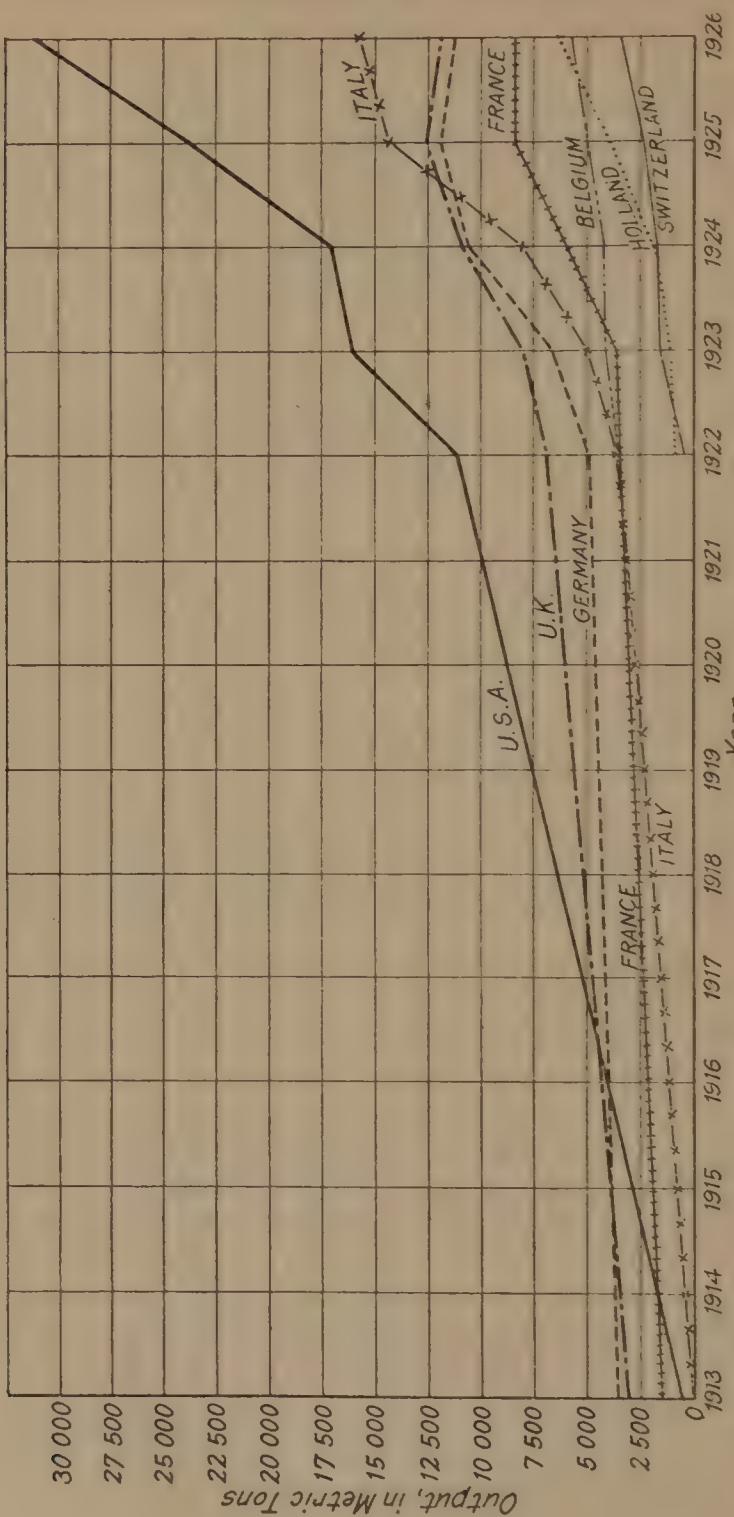

FIG. 49.—Production of Artificial Silk in various countries, 1913–1926.

Up to a few years ago home production was short of home consumption in the chief European countries and the United States, but it increased so rapidly that, internal consumption being satisfied, a very large export trade was built up in Europe. The placing of tariffs, however, on imports of artificial silk in order to protect the home industry compelled the exporting countries to stimulate home consumption and to develop new markets. The largest markets remaining to be developed are the Asiatic countries and South America. It is, therefore, quite likely that the production of artificial silk will steadily increase, provided facilities for working up the product develop *pari passu*.

As has already been stated, practically 90% of the world's output of artificial silk is being made by the viscose process. The displacement of the old cuprammonium and nitrocellulose processes by the viscose process has been very rapid within the last fifteen years, and the majority of the new undertakings propose working this process. This has largely been due to the cheapness of the raw materials—wood-pulp, caustic soda, and carbon bisulphide. On the other hand, the acetate process, although producing a different, and in some respects a superior, product, has had to contend against the considerably higher price of the raw materials used, such as cotton, acetic anhydride, and acetone. The survival of any new process will, therefore, largely depend on the cost of the raw materials used and the quality of the product produced in comparison with the viscose process and product.

Artificial silk has now taken a definite place in the textile industry, and within the next few years its consumption is likely to attain a degree of stability in each country. Apart, however, from variations in fashions and development in its use, it is unlikely that the future will see any phenomenal increase in consumption in those countries where production is now

overtaking the demand, though the world's output appears certain to increase until the markets of the non-producing countries have been fully developed.

The price of artificial silk (viscose) has now reached its pre-war level, but to-day's product is a considerable improvement on that offered then. The following table (taken from the *Times Artificial Silk Supplement*, *April* 2, 1927) shows the fluctuation in price of artificial silk in comparison with other fibres :—

Fibre	1913	1919	1920 (Feb.)	1920 (Oct.)	1926	1927
	Price per lb.					
Artificial silk (viscose), 150 denier	5/3	16/–	19/3	12/6	6/–	5/–
Canton silk (discharged) (common sizes)	17/4	59/8	104/–	46/8	31/4	23/–
Italian silk (discharged) (common sizes)	21/4	73/8	126/11	59/4	40/8	36/–
Egyptian mercerised cotton (= 151 denier)	2/1	7/10	17/5	7/4	4/2	3/5½
Botany worsted (= 159 denier)	3/6	17/6	20/–	12/–	6/9	6/7

As one of the largest manufacturers of artificial silk in this country has recently stated, artificial silk to-day is on its merits by far the cheapest—or " best value "—of any known fibre (3).

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APPENDIX

A. Laboratory Methods used for controlling the Manufacture of Viscose

Wood or Cotton Pulp.

Moisture.—Ten grams of the sample are dried at 102°–105° C. for 6 hours. The loss in weight gives the moisture.

Ash.—The dried sample is ignited in a platinum dish, and the inorganic residue is weighed.

Ether Extract.—Twenty grams are extracted in a Soxhlet tube for 6 hours, and the residue left after distilling off the ether and drying at 100° C. is weighed.

α-Cellulose.—3·5 grams of the wood pulp, previously dried at 105° C. and extracted with ether, are treated with 50 c.c. of 17·5% sodium hydroxide at 18° C. for 45 min. Fifty cubic centimetres of water are then added, and the whole filtered on a Buchner funnel, the cellulose being washed with 200 c.c. of 8% sodium hydroxide. (The alkaline filtrates are made up to 500 c.c. and kept for determination of β- and γ-cellulose, *vide infra.*) The residue is then acidified with 50 c.c. of 5% acetic acid, well washed with hot water, dried at 105° C., and weighed. The weight obtained is that of the α-cellulose (1).

β- and γ-Celluloses.—Fifty cubic centimetres of the alkaline filtrate are treated with 10 c.c. of potassium dichromate solution (90 grams per litre) and 100 c.c. of 72% sulphuric acid. The solution is boiled for 5 min., then cooled and titrated with a standard solution of ferrous ammonium sulphate, using potassium ferricyanide as external indicator. From the amount of potassium dichromate used the quantity of cellulose

(β and γ) present in the solution is calculated from the following equation :—

$$4K_2Cr_2O_7 + C_6H_{10}O_5 + 16H_2SO_4 \longrightarrow 4K_2SO_4 + 4Cr_2(SO_4)_3 + 21H_2O + 6CO_2,$$

from which it will be found that 1 gram $K_2Cr_2O_7$ is equivalent to 0·1375 gram cellulose.

γ-Cellulose.—One hundred cubic centimetres of the alkaline solution are neutralised with sulphuric acid, the precipitated cellulose (β) is filtered off, and the filtrate is oxidised with acid potassium dichromate as before.

From the amount of potassium bichromate used the γ-cellulose is determined. The β-cellulose is then found by difference.

The foregoing method can be varied in several respects, and the results may vary accordingly, but comparable results may be obtained if the method is carried out under standardised conditions. Little is known as to the nature of the β- and γ-celluloses, but the method of analysis serves as a rough means of distinguishing between the cellulose insoluble in 17·5% sodium hydroxide solution (α), acid-precipitated cellulose (β), and other oxidisable impurities (γ).

Alkali Cellulose.

Alkali.—Five grams of the crumbs are treated with 50 c.c. of distilled water, well mixed and titrated with N H_2SO_4, using phenolphthalein and methyl orange as indicators. From the volume of acid used the percentage of sodium hydroxide and carbonate can be calculated.

α-Cellulose.—The cellulose is filtered on a tared filter, washed with boiling water till free from salts and acid, and then dried at 105° C. for 6 hours. The weight multiplied by 20 gives the percentage of α-cellulose.

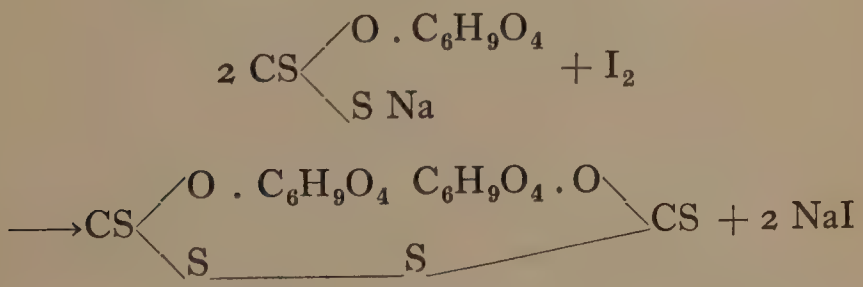
Viscose (2).

Alkali.—Three grams of the viscose are weighed out into a beaker or flask, and then treated with 30 c.c. of distilled water. Ten cubic centimetres of N H_2SO_4 are slowly added. After well shaking the flask, the contents are warmed on a water bath for 10–15 min., cooled, and the excess of acid titrated with N NaOH, using methyl orange as indicator. From the amount of acid used the alkalinity of the viscose, calculated as NaOH, can be determined.

Cellulose.—Four grams of the viscose are weighed out on a flat glass plate and the viscose dried off on a water bath. The film of decomposed viscose thus obtained is soaked off by treatment with a saturated salt solution, and the sulphur compounds are decomposed by treatment with dilute hydrochloric acid. After washing well, the film is dried at 100° C. and weighed.

Total Sulphur.—Twenty-five grams of the viscose are diluted to 250 c.c. with distilled water, and 25 c.c. of the solution are oxidised on a water bath for several hours with an excess of a strong solution of sodium hypochlorite. The solution is acidified with hydrochloric acid, and after the excess of chlorine has been boiled off the oxidised sulphur is determined as barium sulphate.

Xanthate Soda.—Cellulose xanthate reacts with iodine in accordance with the following reaction :—



This reaction has been suggested by Cross as a method for determining viscose.

Owing, however, to the presence of sulphides and other sulphur by-products, which also react with iodine, the method as proposed by Cross is difficult to apply.

The following method, worked out by the author, has been found to give more satisfactory results. Fifty grams of viscose are diluted to 500 c.c., and purified carbon dioxide is bubbled through 100 c.c. of the solution, cooled to 0° C., till no further smell of sulphuretted hydrogen or carbon bisulphide can be detected ($\frac{3}{4}$–1 hour). The solution is then diluted to 200 c.c.; 100 c.c. are treated with 15–20 c.c. of $\frac{N}{10}$ iodine and 25 c.c. of 10% acetic acid in a stoppered bottle, and allowed to stand 15 min. The excess of iodine is then estimated by titration with $\frac{N}{10}$ sodium thiosulphate, using starch as indicator. It is necessary to shake vigorously near the end-point. The other 100 c.c. of the solution is treated with 150 c.c. of a saturated solution of sodium chloride, the separated cellulose xanthate is filtered, and an aliquot portion of the filtrate is treated with 5 c.c. of $\frac{N}{10}$ iodine and 25 c.c. of 10% acetic acid, the excess of iodine being estimated as before. By subtracting the amount of iodine used in the second operation from that used in the first, calculated to equivalent volumes of solution, the amount of iodine reacting with the cellulose xanthate to form cellulose dithiocarbonate is obtained, and from it the sulphur combined as cellulose xanthate, which can be expressed as the xanthate soda per 100 grams cellulose (see p. 23, Chapter III.).

Degree of Ripening.—In order to determine the degree of ripening of viscose, the two tests most usually employed are the " salt-point " and ammonium chloride tests (Hottenroth).

(*a*) *Salt-Point* (3).—The salt-point is the percentage concentration of a sodium chloride solution which is just sufficient to coagulate a single drop of viscose. The test is usually carried out by dropping about 0·1 c.c. of viscose into 20 c.c. of the salt solution. The drop is rapidly mixed with the solution, and the solution is then examined to see whether the viscose has disappeared or coagulated.

It is generally found that a new viscose has a salt-point of 13, and a ripened viscose suitable for spinning of 6 to 3.

(*b*) *Ammonium Chloride Figure* (4).—The ammonium chloride figure is determined by titrating viscose with a standard solution of ammonium chloride till coagulation takes place.

Twenty grams of viscose are diluted with 30 c.c. of distilled water, and 10% ammonium chloride is run into the solution slowly while stirring vigorously. A new viscose usually requires 13–12 c.c. of the solution ; a spinning viscose may require 6–8 c.c.

A similar test has also been suggested using 5% acetic acid in place of the ammonium chloride solution.

Viscosity (5).—The viscosity of viscose (and also of cuprammonium, nitrocellulose and cellulose acetate solutions) can be most conveniently and accurately determined by the falling-sphere viscosimeter described by Gibson and Jacobs.

The method consists in measuring the time taken for a steel ball (0·15 cm. diameter) to travel between two or more fixed graduations on a standard tube. A full description of the apparatus and the method of carrying out the determination will be found in the original paper (5).

B. Physical Tests of Artificial Silk

Determination of Denier.—For the determination of denier special quadrant balances, graduated in deniers, are made, upon which the skeins of a given length can be accurately weighed. In the laboratory a

sensitive chemical balance can be used for determining the denier by weighing short lengths of thread.

Determination of the Twist.—The twist of artificial silk is determined in a machine known as a twist tester. A typical machine is shown in Fig. 50. A length of thread up to 12 inches is fixed between the two screw-clamps at each end of the apparatus. By turning a wheel the thread is untwisted and the amount of the right or left-hand twist is recorded on the dial shown at the right-hand end. The twist is expressed as turns per inch or per metre.

Determination of Tenacity and Elongation.—See Chapter X., p. 87.

Cross Sections.

In order to prepare cross sections of artificial silk, a portion of the thread is embedded in paraffin wax (m.pt. 60° C.). The sections of wax are cut in a microtome and the thread set with gelatine or canada balsam, the wax being subsequently removed by an organic solvent.

C. Identification of Artificial Silks by Chemical Tests

The identification of the different artificial silks is often a matter of importance. A considerable number of chemical tests for this purpose have been suggested, but they do not always give a positive indication, as samples of artificial silk made by the same process may give considerably divergent colours with the different reagents. At the same time, with practice and experience, the results, taken in conjunction with the physical tests (strength, cross-sections, etc.), can be of considerable value in determining the process by which the artificial silk has been manufactured.

The various tests and the general reactions given by the different varieties of artificial silk are shown in the subjoined table.

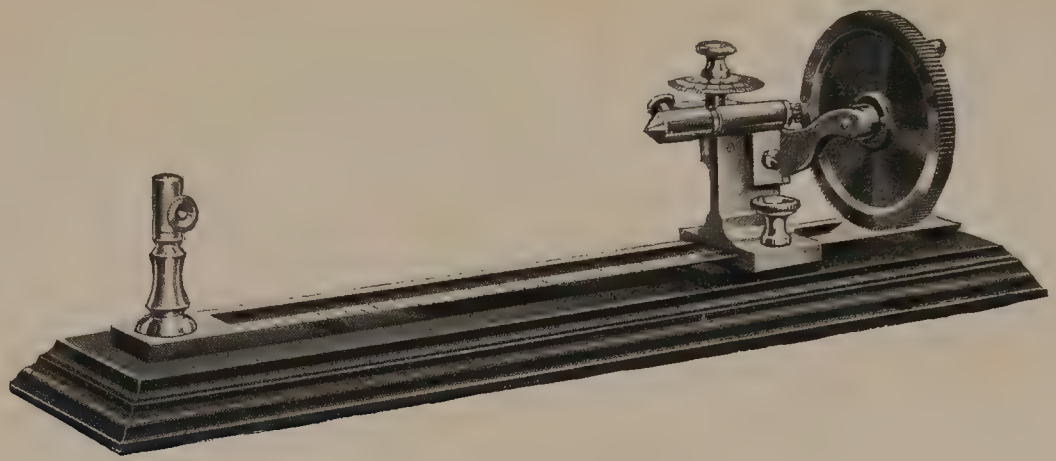


FIG. 50.—Twist Tester.

(*Goodbrand & Co., Ltd., Stalybridge.*)

[*To face p.* 138.

Summary of Chemical Identification Tests for Artificial Silks

Variety of Artificial Silk	Behaviour on ignition (7)	Solution of iodine in potassium iodide (7)	Chemically pure sulphuric acid (8)	Diphenylamine in pure sulphuric acid	Ammoniacal silver nitrate (7)	Alkaline silver nitrate.* Boil solution for 1 min. (9)	Ruthenium Red (10)	Acetone (7)	Chloroform (7)	Very dilute methylene blue solution (11)	Naphthylamine Black 4.B. (9)
Viscose .	Burns like cotton, leaving only a fine white ash	Greenish-blue	Reddish-brown ; in ¾–1 hour rusty-brown	No colour	Reddish-brown	Dark brownish-black	Bright pink	Insoluble	Insoluble	Light blue	Light reddish-grey
Nitrocellulose		Reddish-blue	Colourless : in ¾–1 hr. pale yellow	Deep navy blue	—	Brown	Bright red	Insoluble	Insoluble	Blue-violet	—
Cuprammonium		Bluish-green	Yellowish : ¾–1 hour yellowish brown	No colour	Unstained	Very light grey	Scarcely coloured	Insoluble	Insoluble	Pale-blue	Dark bluish-grey
Cellulose acetate	Burns like natural silk, leaving a cinder	Reddish-brown	—	No colour	—	—	Slightly and irregularly stained	Soluble	Soluble or forms a gel	Not coloured	—

* Reagent consists of : 1 per cent. $AgNO_3$; 4 per cent. NaOH ; 4 per cent. sodium thiosulphate.

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